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(54) Title: METHOD AND APPARATUS FOR FORMING A FILM ON A SUBSTRATE

(57) Abstract: This invention relates to a method and apparatus for forming a film on the substrate. The method comprises supplying to the chamber in gaseous or vapour form a silicon containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate and setting the film such that carbon containing groups are retained therein. In particular embodiments the setting is achieved by exposing the film to H₂ plasma.

Method and Apparatus for forming a Film on a Substrate

This invention relates to a method and apparatus for forming a film on a substrate particularly, although not exclusively, to a film which is deposited on a semiconductor silicon wafer with flowing properties and retains carbon-containing groups on setting.

A number of methods have been disclosed for depositing a thin film on a semiconductor wafer, and examples included US 5314724, US 489753, US 5593741, EP-A-0731982 and EP-A-0726599. It can be seen from these that, up until recently, organic-containing silicon precursors have been processed or further processed in such a way as to avoid or subsequently remove organic components from the as-deposited film; this is, for example, disclosed in US 5314724. In addition, for some applications, it has been found to be difficult to retain both good film quality and good gap-fill capability on the surfaces and in recesses of a wafer on which the film is deposited.

According to a first aspect of the present invention, there is provided a method of forming a film on a substrate comprising:

- (a) positioning the substrate on a support in a chamber;
- (b) Supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and
- (c) setting the film such that carbon-containing groups

are retained therein.

The present invention provides a method of forming an unset film. Typically, the film is flowable (that is a film with a degree of surface mobility) and may thus provide good gap fill properties on the substrate.

It should be understood that without affecting the generality of this invention where gap fill properties are not required, e.g. for InterMetal Dielectric (IMD) layers on a semiconductor, then a flowing intermediate film will not be required. However the intermediate film deposited according to this invention will contain OH, which is almost entirely removed by the 'setting' process.

The formation of an OH and CH containing intermediate which is then further processed to remove OH but contain CH enables the formation of improved dielectric layers.

The substrate may be a semiconductor wafer, for example a silicon semiconductor wafer of the type known in the art.

Preferably, the oxidising agent is oxygen, although others could be used, for example H₂O₂.

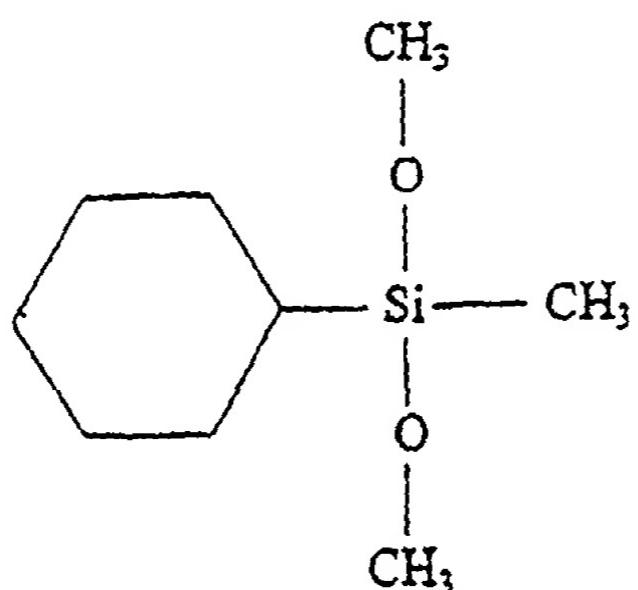
For example, the silicon-containing organic compound may be an organosilane or an organosiloxane. Preferably, the silicon-containing organic compound is an alkylsilane, and even more preferably is a tetraalkylsilane. In a particularly preferred embodiment of the invention, the silicon-containing organic compound is tetramethylsilane (TMS). However, for example, other organosilanes or

organosiloxanes could be used, one example being 1,1,3,3-tetramethyldisiloxane (TMDS).

Experiments suggest that methoxysilanes, and in particular methoxymethyilsilanes, produce films with very low dielectric constants and may be particularly preferred.

Particularly good results have been achieved with cyclohexyldimethoxymethyilsilane (CHDMMS) which has the following structure:

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Experiments have also shown that a methoxysilane (e.g. CHDMMS) may be able to be processed as in the above method described, but without any oxidising agent present in the plasma. It is supposed that this is because the Si-O bond already exists as part of the methoxy group.

Accordingly, according to another aspect the invention consists in a method of forming a film on a substrate comprising:

- 5 (a) positioning the substrate on a support in a chamber;
(b) supplying to the chamber in gaseous or vapour form an organic compound including an Si-O bond to deposit a

film on the substrate; and

- (c) setting (e.g. annealing) the film such that carbon-containing groups are retained therein.

Preferably the compound is supplied in the presence of a plasma, but other energy sources may be utilised to cause appropriate deposition and these may be combined with spin-on techniques.

The film may be deposited on a substrate positioned on a low-temperature support for example, a support at a temperature of about 0°C. Indeed temperatures in the range 0°C to 70°C have produced practical results, with temperatures of 30° and 50°C proving particularly practical.

In one embodiment, the method may further comprise supplying RF power during deposition of the film. This RF power is preferably applied to a showerhead or the like through which the gaseous precursors are passed into the chamber.

Whilst any suitable experimental conditions may be used, it has been found that typical conditions include a flow rate of 210 sccm tetramethylsilane, a flow rate of 200 sccm O₂, a chamber pressure of 2000 mT, a support temperature of 0° and a showerhead temperature of 100°C, and 250 watts of 380 khz RF power applied to the showerhead, although it is pointed out that these are only typical conditions.

The setting of the film may be carried out by an

annealing step, for example at a temperature of about 450°C which serves to remove water from the deposited film. It has been found that typical k value of the set film is about 2.55, for example for a 6000Å thick film deposited with a base layer (prior to deposition of the film) or capping layer (on the formed layer) after an annealing step at about 450°C in the absence of oxygen. This k value is a measure of the dielectric constant and it can be seen that the present invention provides a particularly low dielectric constant.

Alternatively, and often preferably, the setting step is performed by exposing the deposited film to an H₂ containing plasma without any prior heating of the film. In this connection it is preferred that the support is not biased during the deposition stage to avoid heating arising from ion bombardment.

According to a third aspect of the present invention, there is provided a method of forming a film on a substrate comprising:

- 20 (a) positioning the substrate on a support in a chamber;
- (b) supplying to the chamber in gaseous or vapour form tetramethylsilane and oxygen in the presence of a plasma and a supply of RF power to deposit a film on the substrate; and
- 25 (c) setting the film such that carbon-containing groups are retained therein.

The setting step can be performed as set out above.

Particularly good results have been achieved with the H₂ plasma treatment without prior heating.

According to a further aspect of the present invention, there is provided an apparatus for forming a film on a substrate, the apparatus comprising:

- 5 (a) a support for the substrate positioned in a chamber;
- (b) means for supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and
- 10 (c) means for setting the film such that carbon-containing groups are retained therein.

The apparatus may, in one embodiment, further comprise means for improving the uniformity of the deposition of the film on the substrate. This may be arranged in the region of, or around, a showerhead and, whilst the applicant is not to be restricted hereby, it is thought that its role in the uniformity of deposition is possibly as a result of providing a site for surface reactions about the surface periphery thus enhancing deposition rate at the edge of the substrate.

20 Although the invention has been defined above, it is to be understood that it includes any inventive combination of the features set out above or in the following description.

25 The invention may be performed in various ways and a specific embodiment will now be described, by way of

example, with reference to the accompanying drawings, an invention which:

Figure 1 is a schematic view of an apparatus for use in the present invention;

5 Figure 2 is a Fourier Transform Infra-Red (FTIR) spectrum showing an as-deposited and annealed film according to this invention;

10 Figures 3(a) and 3(b) are scanning electron micrographs showing the annealed film formed by the present invention;

Figure 4 is a Fourier Transform Infra-Red (FTIR) spectrum for a first process run without oxygen;

Figure 5 is the equivalent FTIR for the process run with oxygen;

15 Figure 6 is a table showing initial experimental results using standard delivery systems for CHDMMS;

Figure 7 is a table showing experimental results using a syringe pump to deliver CHDMMS;

20 Figures 8 to 10 are FTIR spectrum relating to certain experiments identified in Figure 7;

Figure 11 shows FTIR plots for film formed from TMS after an anneal (FTM) process and after H₂ plasma processing when no anneal step has occurred;

25 Figure 12 is a graph of plots showing the affect of an FTM process, a 5 min H₂ plasma and a 10 min H₂ plasma on the thickness and the refractive index of a TMS based film;

Figures 13 to 15 are respective bar graphs indicating

the affects of an oxidising strip on FTM, 5 min H₂ plasma and 10 min H₂ plasma treated TMS + O₂ deposited films;

Figure 16 illustrates the film stress values pre- and post-oxidising strip, after various post film formation treatment regimes;

Figure 17 sets out the dielectric constant of TMS films after various post formation regimes;

Figure 18 is a bar graph comparing the dielectric constant of layers treated by FTM, 5 min, 10 min and 30 min H₂ plasma for a pair of substrates; and

Figure 19 is a SIMS plot for a TMS + O₂ deposited film which has been set with a 5 min H₂ plasma.

Referring to Figure 1, there is shown an apparatus generally at 1 which includes a vacuum chamber 2 having a showerhead 3 and a wafer support or platen 4. The showerhead 3 is connected to an RF source (not shown) to form one electrode, whilst the support 4 if preferably earthed. Alternatively or additionally, the RF source could be connected to the support 4. The showerhead 3 is connected via pipes (not shown) to respective sources of tetramethylsilane and oxygen. The apparatus is generally of the form disclosed in EP-A-0731982, which is incorporated herein by reference. However, a standard (non-duplex) showerhead is normally used. Also shown is an optional uniformity ring 5 arranged around the showerhead 3. This ring 5 plays an active role in the uniformity of deposition of the film on the wafer and may be desirable

for some processes.

In use, the apparatus 1 is arranged to deposit a water and/or OH containing intermediate layer on a wafer which may be flowable and may be used to produce a planar layer or for "gap filling" for applications such as pre-metal dielectric, shallow trench isolation and intermetal dielectric on semiconductor devices. The film is formed by introducing into the chamber tetramethylsilane and oxygen in gaseous or vapour form and reacting them within the chamber. This forms an intermediate layer with a degree of surface mobility even when a plasma is present. It has been found that very small dimensioned gaps can be filled by the process of the present invention. This is not to restrict the invention as often process conditions may yield an intermediate layer containing OH that does not flow but still retains the other characteristics of this invention. The reaction takes place in the presence of a plasma. Subsequently, the film is annealed by heating, preferably in the absence of oxygen and most preferably in the presence of a hydrogen containing plasma.

Example

The precursor tetramethylsilane (TMS) has been applied with various other precursors, a platen temperature of approximately 0°C and RF power of either low (e.g. 380 KHz) or high (e.g. 13.56 Mhz) frequency where indicated. The basic results were as follows:

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- TMS + H₂O₂ No deposition in the pressure range up to 5,000 mT
- 5 TMS + MeSiH₃ + H₂O₂ Slight increase in carbon content over just MeSiH₃ + H₂O₂. Deposition rate ~ 6000 Å/min
- TMS + DiH₄ + H₂O₂ No carbon in the film. Deposition rate ~ 900 Å/min
- TMS + H₂O₂ + RF Deposition rate ~ 400 Å/min. High refractive index
- 10 TMS + O₂ + RF Deposition rate over 2 micron/min - high carbon content.
- A 'preferred' process was then developed consisting of:
210sccm TMS (calculated from fill rate checks)
200sccm O₂
- 15 2,000 mT pressure
0° platen temperature and 100°C showerhead temperature
250 watts of 380khz RF power applied to the showerhead.
This yielded a k value of 2.55 (measured by CV techniques)
for a 6,000 Å thick film deposited without base or capping
- 20 after an anneal at approximately 450°C in the absence of oxygen.

Figure 2 shows a FTIR spectrum for an as-deposited and annealed film according to this aspect of the invention. The two spectra are shown overlain on the same diagram for ease of comparison. The as-deposited spectrum is the lower of the two and shows at 6 the characteristic peak of O-H bonds associated with water. Between 3,000 and 2,600 wave

numbers O-H bonds associated with free water, isolated O-H and H bonded O-H are present. Water contains free water and H bonded O-H and thus gives a characteristically broad peak in this area. At 7 is the C-H₃ peak; at 8 is the Si-CH₃ peak (Si-C); and at 9 is the Si-O peak.

It can thus be seen that a film has been deposited containing water and/or OH which is subsequently removed by the annealing step and that CH₃ is present, is bonded to Si and remains in the film after annealing to form the hard film.

Generally, an indicator of low k characteristics is a high Peak Area Ratio(PAR) between Si-C and Si-O on the FTIR. It is believed Si-C bonds block Si-O bonds and thus reduce the density of the resultant film. Hence, a high Peak Area Ratio Si-C:Si-O is indicative of a low k film. It was however noted that for these plasma deposited and annealed films the measured k values were not as low as the Peak Area Ratio Si-C:SiO would suggest from non-plasma deposited low k films deposited from a reaction of methylsilane and peroxide.

Films of this invention as annealed as shown in Figure 3 which demonstrate the flowing characteristics of the as-deposited film.

In general, the following effect of changing the parameters in a process have been observed:

	<u>Parameter</u>	<u>Property</u>			
		<u>Refractive Index</u>	<u>FTIR Peak SiC/SiO</u>	<u>Area Ratio CH/SiO</u>	<u>Uniformity</u>
5	Pressure increase	down	up	up	better
	Power increase	none	down	down	better
	Nitrogen flow increase	up	down	down	worse
	TMs/O ₂ ratio increase	down	up	up	none
	Total TMS/O ₂ decrease	none	down	down	none

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An experiment has particularly been carried out using cyclohexyldimethoxymethylsilane (CHDMMS). As is reported below this has shown significantly reduced dielectric constants. It is anticipated that benefits will be found from many methoxysilane compounds such as tetramethoxysilane.

The experiments were carried out in a chamber substantially as shown in Figure 1, or in our co-pending British Patent Application 9914879.3, with an electrode gap spacings of 40mm and 20mm and the uniformity ring shield used for non-plasma based processes removed. The CHDMMS was fed into the chamber using a syringe delivery system described in our co-pending British Patent Application No. 9922691.2, which is incorporated hereinby reference, as opposed to a traditional low vapour pressure mass flow controller. This was done due to the fact that, as described below, CHDMMS could not be reliably delivered by conventional means as it has a relatively high boiling point (approximately 200°C) compared to most of the other precursor materials investigated in Application 9914879.3.

All processes were run with plasmas applied to the

showerhead. All wafers were 'set' by annealing for typically 30 minutes at approximately 480°C.

The following parameter ranges have been investigated:

5	Pressure	-	500 mT to 1500 mT
	Power (380 kHz)	-	50 W to 750 W
	Platen temperature	-	0°C to 70°C
	CHDMMS flows	-	0.5 g/min to 1.5 g/min
10	Oxygen flows	-	0 to 200 sccm
	Nitrogen flows	-	0 to 400 sccm
	Peroxide flows	-	0 to 0.75 g/min

It will be appreciated that the relative flow rates are particularly relevant to the process. In general higher rates lead to higher deposition rates and thus a broad range of flow rates can achieve similar results. Thus values outside the above ranges may be applicable.

Two particularly preferred process examples are given below: one of these is with oxygen and one is without oxygen.

Process 1 (no O₂)	
Pressure	900 mT
Power	500 W
Platen temperature	50°C
CHDMMS flow	0.85 g/min
Nitrogen flow	200 sccm

Process 2 (with O₂)	
Pressure	900 mT
Power	250 W
Platen temperature	50°C
CHDMMS flow	0.85 g/min
Oxygen flow	50 sccm
Nitrogen flow	150 sccm

The resultant films were annealed and the post anneal results were as follows:

Process 1 (no O₂)	
Deposition rate	17000Å/min
Uniformity (max/min)	± 4%
Refractive index	1.370
Dielectric constant	2.55

Process 2 (with O₂)	
Deposition rate	9500Å/min
Uniformity (max/min)	± 5%
Refractive index	1.340
Dielectric constant	2.25

5 As can be seen the dielectric constants in each case are desirably low, but the "with oxygen" process is significantly advantageous.

Figures 4 and 5 show the respective FTIR spectra post anneal. It will be seen that they are substantially 10 similar. The feature between 2500 and 2000 in Figure 5 is believed to result from atmospheric (background) CO₂.

In fact, initial experiments were carried out using a CHDMMS source consisting of a PTFE pot within an evacuated aluminium vessel which was heated to 150°C. The pot was 15 connected by gas line to a gas mass flow controller suitable for H₂O with a conversion factor of 1.000. The RF power was applied to the showerhead with a spacing from the wafer of 40mm. The RF was 380khz continuous mode. Results from these experiments are shown in Figure 6. The numbers

in the CHDMMS column are the nominal gas flow as measured by the mass flow controller however stable flows could not be achieved and therefore these results are for near random quantities of CHDMMS being delivered to the process chamber. At this point experimentation was halted until a superior delivery system for this precursor could be developed.

CHDMMS has a boiling point of 201.2°C, and a density of 0.940 g/cc. As it was noted in these experiments that CHDMMS deposits a low k insulator without the addition of an oxidising agent it is therefore possible that it could be delivered as a liquid to a semiconductor wafer without a chamber being required (e.g. by well known 'spin-on' techniques) and then reacted either thermally or by plasma to form a low k ($k<3$) insulator layer. The apparatus used may in effect deposit a liquid by vaporising the liquid precursor, delivering it as a vapour and then condensing it onto the wafer at a temperature below the boiling point of the precursor at that pressure. It is not yet clear if the reactions to the precursor take place on the wafer or at some other place, depositing reaction products onto the wafer.

Having developed a more suitable liquid delivery system which utilises a syringe pump, further experiments

were carried out as shown in Figure 7. From these experiments preferred processes were developed as further described here. FTIR for runs 13, 14 and 16-23 of Figure 6 respectively are illustrated in Figures 8 to 10.

5 Further experiments have been carried out using the following conditions:

Pressure:	2500 millitorr
RF Power at 13.56 Mhz	250 watts/200mm wafer
Showerhead temperature	100°C
10 TMS flow	100sccm (approximately)
Oxygen flow	100sccm
Nitrogen flow	500-600sccm

15 The ratio of TMS (tetramethylsilane) to oxygen is the same as previously (approximately equal quantities), but at half the total flow rates. In this preferred process nitrogen has been used, primarily as a dilutant.

20 Thermal treatment step ("setting" or "anneal")
Time 5 minutes
Pressure 10 torr nitrogen (no oxygen)
Wafer temperature 400°C approximately

25 In the process above, where the process platen temperature was varied, the results were as follows

	T Rate °C	Non-Uniformity Å/min	FTIR SiC/SiO	FTIR SiH/SiO	FTIR CH/SiO	RI av.	Dielectric constant
30	10	7,778	2.7	0.0608	0.0060	0.0287	1.3825
	20	7,673	3.8	0.0594	0.0057	0.0280	1.3832
	30	7,589	4.8	0.0588	0.0059	0.0282	1.3791
	45	7,543	3.1	0.0584	0.0056	0.0273	1.3867
	55	not recorded		0.0527	0.0044	0.0234	not recorded
	60	6,968	3.9	0.0512	0.0074	0.0293	1.3935

Once more the initial deposition process puts down a water and/or OH containing intermediate film which needs to be set to substantially remove the water and/or OH to create a low k layer. For the purposes of the above

experiment this setting was achieved by a thermal treatment step as indicated. However other post deposition processes have been experimented with, as can be seen below. The significant features of this experiment were both the continued achievement of a dielectric constant below 3 and the observation that both the refractive index (which is believed to be a measurement of density) and the dielectric constant dipped when a platen temperature of 30° was used. These results are consistent with the normal understanding that dielectric constant and density are related for a specific film composition, so that lower refractive index will normally indicate a lower dielectric constant.

Subsequent to this experiment a further set of films were formed using the following process matrix:

15	• TMS	-	100 sccm
	• O2	-	100 sccm
	• N2	-	600 sccm
	• Pressure	-	2000 mT
	• Substrate support-		30°C, DC ground potential
20			(unbiased)
	• Power	-	250 Watts High Frequency 13.56 MHz to the showerhead

The films resulting from this process were set either by the annealing process (which is hereinafter referred to

as FTM treatment) or process and/or by treating the film with an H₂ plasma treatment.

The FTM process was as follows:

- Wafer temperature 450°C
- 5 • Pressure 10 Torr (Nitrogen)
- Time 3-5 minutes

The H₂ plasma treatment was as follows:

- Hydrogen - 1000 sccm
- Pressure - 4000 MT
- 10 • Temperature - 400°C
- Power - 2000 Watts High Frequency 13.56 MHz
 to an electrode opposed the wafer
- Time - Depends on thickness but typically 3
 minutes for 6kÅ although longer times
15 appear to lead to lower K.

Alternatively other RF frequencies could be used applied to any electrode or electrodes either internal or external to the wafer containing chamber such as to create or sustain ionised hydrogen species adjacent to the film to be treated. This is to include remote plasma sources including microwave and inductively completed RF sources wherever situated.

The H₂ plasma may also contain other components e.g. effectively inert dilutants for example argon, helium or

other gasses or vapours that do not detract from this treatment.

Figure 11 shows respective FTIR plots for the film prepared as described above and then treated by FTM or by plasma. Beneath each chart is an indication of the bonding ratios between various components. As will be understood by a man skilled in the art the slope of the graph is not relevant in a FTIR plot; it is only the peaks which provide information. The relative heights of the peaks are indicated by the ratio tables and it will be seen that there is a significant reduction in the bonding between the various components in a plasma treated film as compared with one that has had the FTM post deposition treatment. This indicates that the hydrogen plasma treated intermediate film is structurally different from the FTM treated intermediate film.

In Figure 12 the upper plot indicates that there is no significant difference in film thickness between the various post treatment processes, but there is a significant driving up of the refractive index the longer a plasma treatment takes place. Indeed after a 10 minute H₂ plasma, the refractive index is approaching that of pure SiO. Normally, as has been explained above, this would be expected to result in a significant increase in dielectric

constant, but as can be seen in Figure 17 an increase in the period of the H₂ plasma treatment simultaneously produces a significant decrease in the dielectric constant, provided that the film is not subject to heat treatment prior to the plasma treatment. Thus after a 10 minute H₂ plasma treatment the OH containing film is set and has a dielectric constant of below 2.2, which is an extremely low figure typically unachievable by chemical vapour deposition means.

It will be noted that a very short H₂ plasma treatment (e.g. 1 minute) does not render the film totally stable nor does it reduce significantly the dielectric constant below an FTM anneal although the film is still comparable with other reported films. Wet etch rate experiments have demonstrated that the hydrogen plasma treatment starts at the top of the film. The longer the plasma process, the greater the depth treated the lower the k value of the treated film. The hydrogen plasma treated film etches considerably (e.g. 20 or more times) slower than the FTM treated film. It will also be observed that an H₂ plasma treatment is also not effective in reducing dielectric constant after a previous heating or anneal step.

Turning now to Figures 13, 14 and 15 it will be seen in Figure 13 that film which has had the FMT treatment

appears to be very susceptible to an oxidising process e.g. a photoresist strip with carbon and hydrogen seemingly being removed from the material. This is not totally surprising, because such an oxidising process was previously used to remove such materials in the film (in particular organics from precursors) before it was appreciated that they might have a beneficial affect on the dielectric constant. Figures 14 and 15, on the other hand, show that the plasma treated films are substantially unaffected by the oxidising photoresist strip process. This is of course important, because it makes it much easier to remove resist from the surface of the dielectric layer without damaging that layer. Figure 16 shows that the plasma treated films also have particularly low stress values whether before or after the oxidising strip.

It is believed that similar results would be achieved with most flowable or water and/or OH containing films that retain carbon, more particularly CH, in the finally used dielectric layers.

Thus the inventors have, in particular determined a process for depositing a flowable or at least OH containing intermediate film which is subsequently set using heat in the absence of oxygen and preferably in the presence of an H₂ containing plasma with the result that the film has a

dielectric constant below 3 and, with the application of hydrogen plasma, a reduced dielectric constant and a good resistance to oxidising strip. It is postulated that this combination results from the surprising fact that H₂ treatment reduces the dielectric constant whilst increasing the refractive index and hence, almost certainly the density as evidenced by a greatly reduced wet etch rate.

Further evidence for this is illustrated in Figures 18 and 19. Figure 18 shows that progressive treatment by H₂ plasma drives down the dielectric constant, with samples treated for 30 minutes achieving a k of 1.8.

Figure 19 provides analysis of the hydrogen plasma treated film has been carried out as follows:

SIMS (secondary ion mass spectrometry) data of a TMS + O₂ deposited film that has been hydrogen plasma treated for 5 minutes has been generated. [The horizontal axis is through the depth of the sample starting at just above the surface and ending in the silicon wafer. What is shown is an organic contaminated (high C) sample surface (to be ignored), followed by a 'true' analysis].

The SIMS profile shows a film surface depleted of carbon and hydrogen by the hydrogen plasma treatment. This is a not unsurprising result and is consistent with a measurable difference in the dielectric constant of this

surface layer and the bulk of the film. When this surface is etched away the remainder of the film (adjusted for it's reduced thickness) has a lower dielectric constant than the whole of the film including this surface layer. Yet the 5 whole film including this carbon depleted surface has a lower k value than an FTM treated film.

Wet etch rate experiments show that the hydrogen plasma treatment commences at the upper surface and progresses through the film. The hydrogen plasma treated 10 film wet etches considerably more slowly than an FTM treated film and thus provides clear evidence that depth of treatment increases with plasma treatment times.

It is postulated that the hydrogen plasma treatment effectively replaces Si-CH₃ in the film with Si-CH₂-Si (by 15 intermediate reactions in which hydrogen ions and radicals play a part) with increased Si-Si linkage responsible for the increase in the refractive index.

CLAIMS

1. A method of forming a film on a substrate comprising:
 - (a) positioning the substrate on a support in a chamber;
 - (b) supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and
 - (c) setting the film such that carbon-containing groups are contained therein.
- 10 2. A method according to claim 1, wherein the oxidising agent is oxygen.
3. A method according to claim 1 or 2, wherein the silicon-containing organic compound is an alkylsilane.
- 15 4. A method according to any preceding claim, herein the silicon-containing organic compound is a tetraalkylsilane.
5. A method according to claim 4, wherein the silicon-containing organic compound is tetramethylsilane.
6. A method according to claim 1 or 2, wherein the silicon-containing organic compound is a methyisilane.
- 20 7. A method according to claim 3, wherein the silicon-containing organic compound is cyclohexyldimethoxymethylsilane.

8. A method according to any preceding claim, wherein the film is deposited on a substrate positioned on a low temperature support.
9. A method according to claim 6, wherein the support is at a temperature between about 0°C to about 60°C.
10. A method according to claim 6 or claim 7 wherein the support is at about 30°C,
11. A method according to any preceding claim, further comprising providing a plasma during deposition of the film.
12. A method according to any preceding claim, wherein the set film has a dielectric constant of about 2.55 or less.
13. A method of forming a film on a substrate comprising:
 - (a) positioning the substrate on a support in a chamber.
 - 15 (b) supplying to the chamber in gaseous or vapour form tetramethylsilane and oxygen in the presence of a plasma to deposit a film on the substrate; and
 - (c) setting the film such that carbon-containing groups are contained therein.
- 20 14. A method according to any preceding claim, further comprising supplying the plasma from an RF power source connected to an electrode opposing the substrate support.

15. A method according to any preceding claim wherein the substrate support is at D.C. ground during the application of the plasma.
16. A method as claimed in any one of the preceding claims wherein the film is set by exposing it to an H₂ containing plasma without any prior annealing or heating step.
5
17. A method as claimed in claim 16 wherein the H₂ containing plasma is substantially only a H₂ plasma.
18. A method as claimed in claim 16 or 17 wherein the H₂ containing plasma treatment last for between 30 seconds and 30 minutes.
10
19. A method as claimed in claim 16 or 17 wherein the H₂ containing plasma treatment lasts from 1 to 10 minutes.
15
20. A method as claimed in claim 16 or 17 wherein the H₂ containing plasma treatment step lasts no more than 5 minutes.
21. A method as claimed in claim 16 or 17 wherein the H₂ containing plasma treatment step lasts no more than 10 minutes.
20
22. A method as claimed in claim 16 where the hydrogen containing plasma is applied simultaneously with heating.

23. A method as claimed in claim 22 where the substrate is heated to approximately 400°C.
24. A method substantially as hereinbefore described, with reference to the accompanying drawings and examples.
- 5 25. A method as claimed in claim 1 where the setting of the film substantially removes water and/or OH peaks from the FTIR spectra of the as deposited film.
26. An apparatus for forming a film on a substrate, the
10 apparatus comprising:
- (a) a support for the substrate positioned in a chamber;
 - (b) means for supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and
 - 15 (c) means for setting the film such that carbon-containing groups are contained therein.
27. An apparatus according to claim 26, further comprising means for improving the uniformity of the deposition of the
20 film on the substrate.
28. An apparatus according to claim 27, wherein the means for improving the uniformity is arranged around a showerhead.

28

29. An apparatus substantially as hereinbefore described with reference to, and as illustrated in, the accompanying drawings.

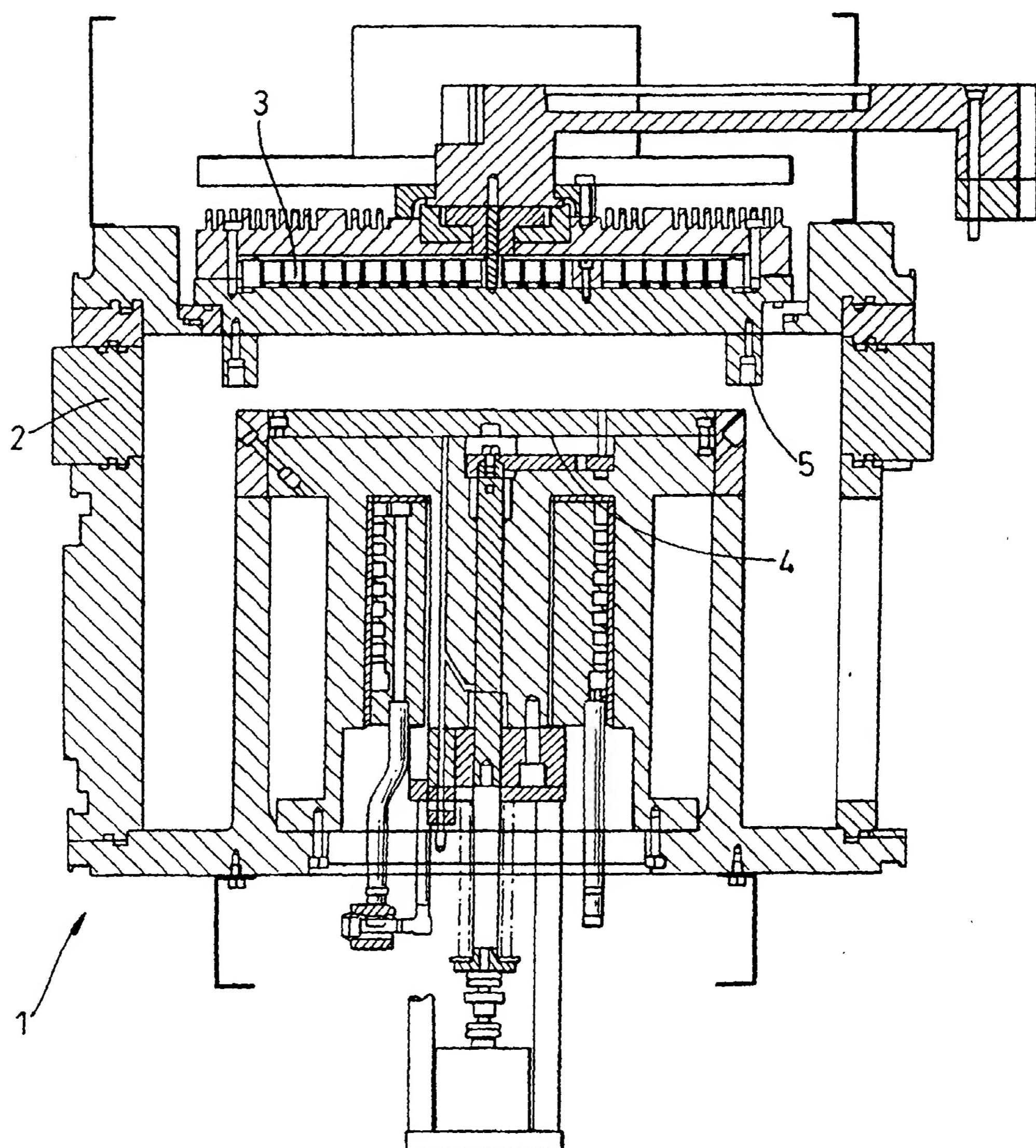
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*Fig 1*

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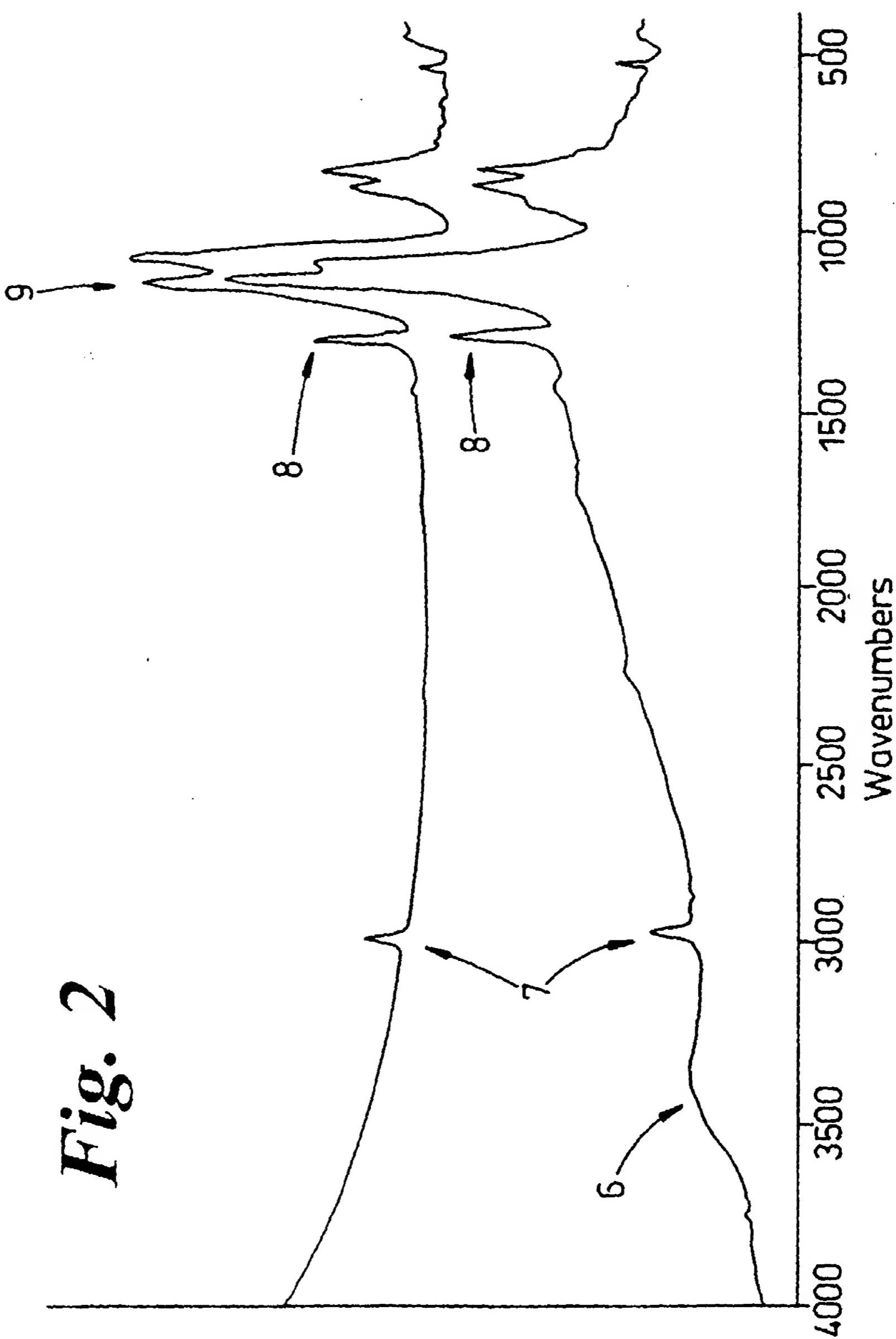


Fig. 2

210 / 200 TMS/CO₂ 20000MT 250 W 0°C PLATEN PRE AND POST ANNEAL

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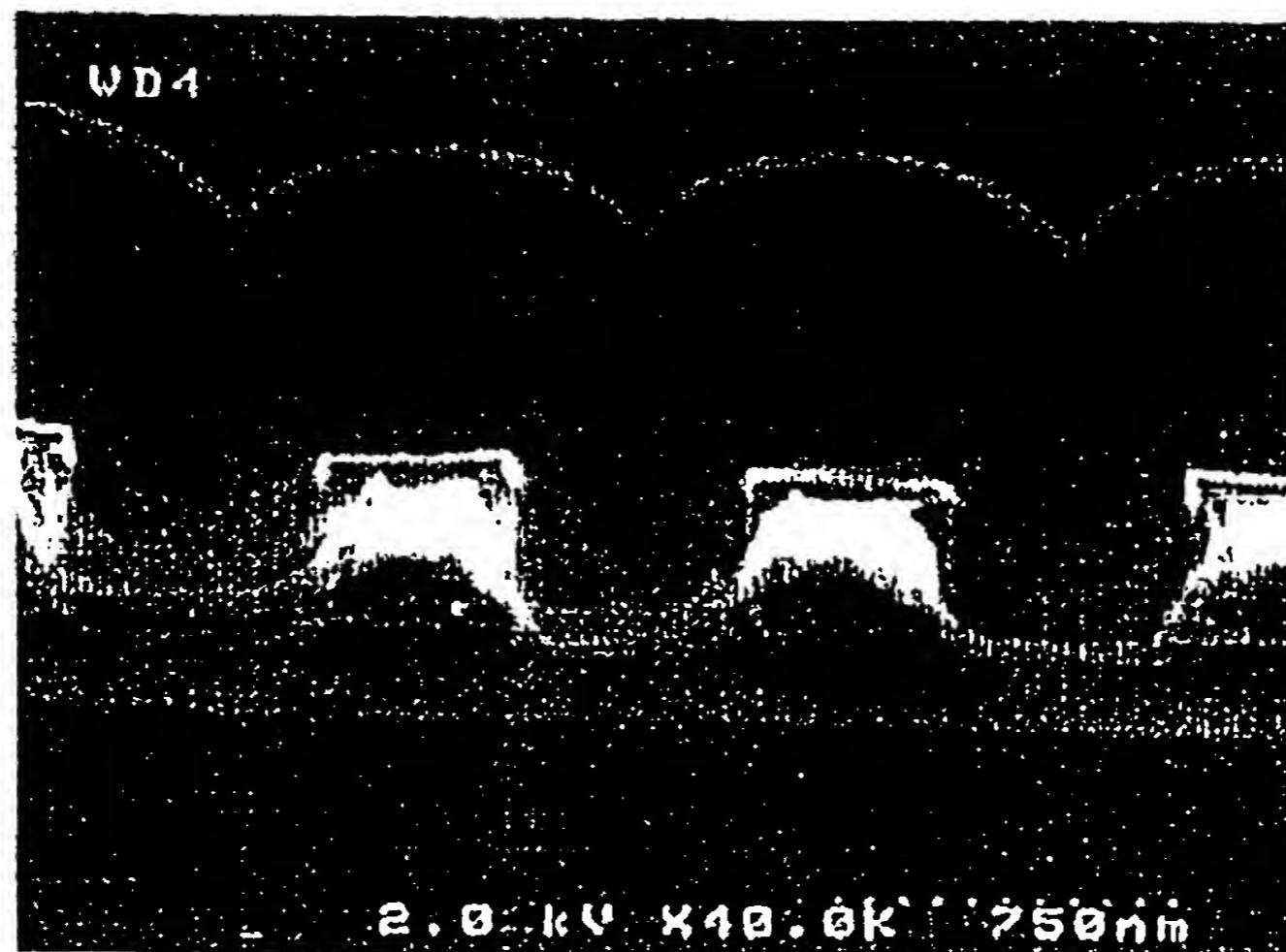


Fig. 3(a)



Fig 3(b)

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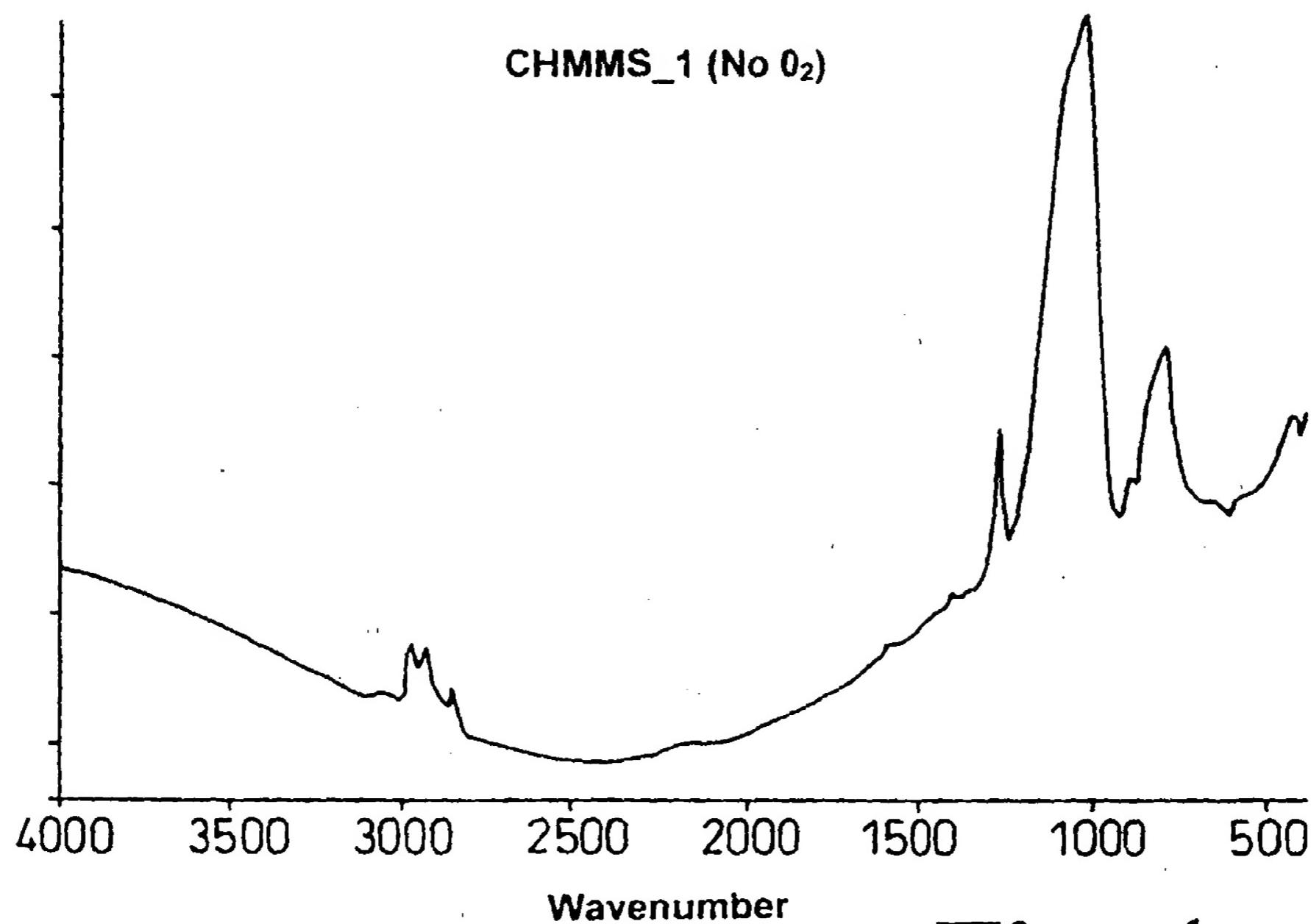


Fig. 4

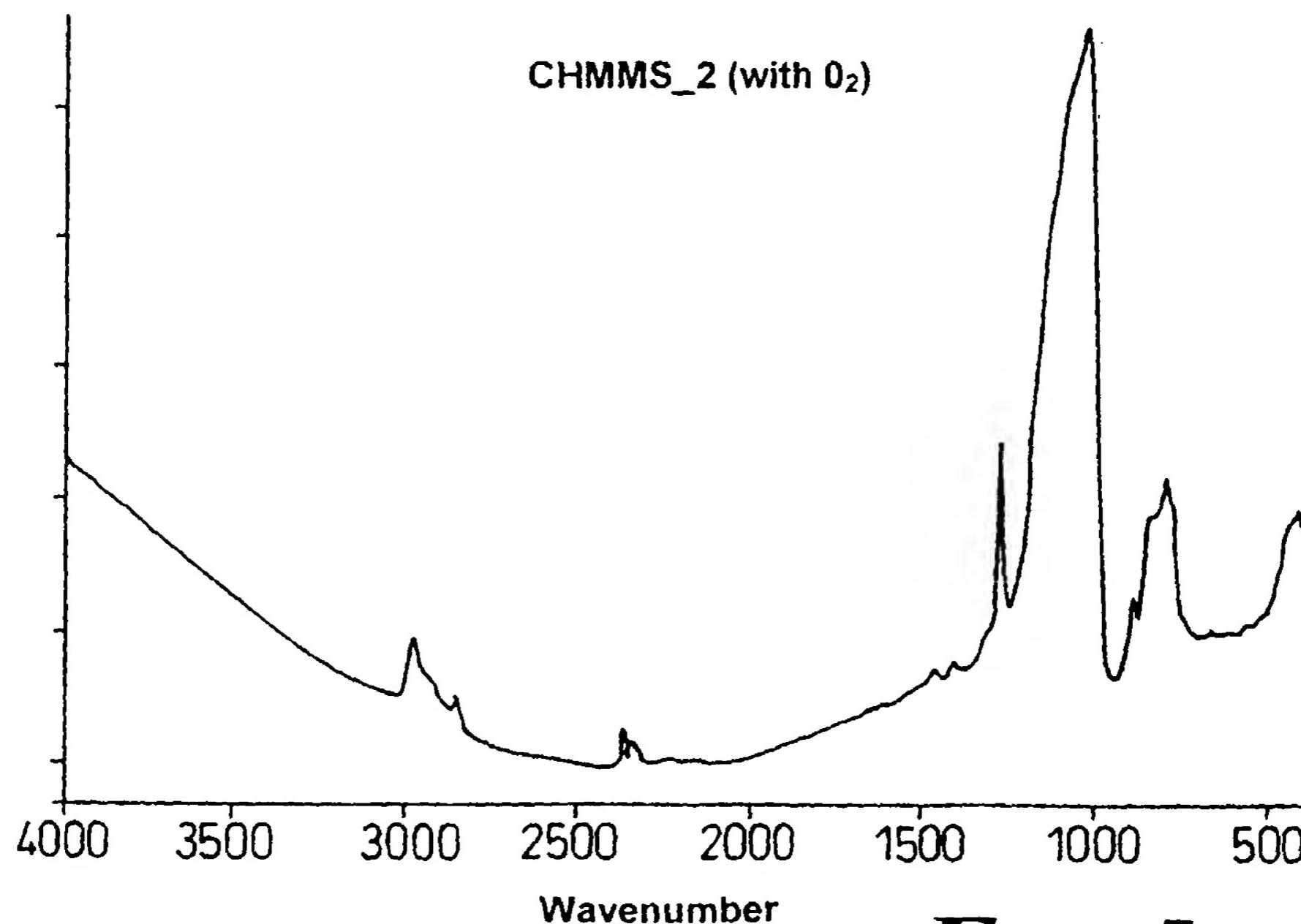


Fig. 5

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Date	Run No	CHMMS	H ₂ O ₂	O ₂	N ₂	RF Power (W)	Pressure (mT)	Platen (°C)	Si/Head (°C)	Dep rate (Å/min)	Uniformity	Rj	Rj Range	SiC/SiO	SiH/SiO	CH/SiO	K
10/05/99	1	1000	0.75	0	0	50	1500	70	100	1166	6.6	1.482	0.0007				
	2	1300	0.75	0	0	50	900	70	100	681	5.1	1.3702	0.0074				
	3	1300	0.7	0	0	100	900	70	100	2542	6.5	1.3321	0.01				
	4	1300	0.7	0	0	100	900	70	100	1853	6.1	1.3676	0.015				
	6	1300	0.7	0	0	100	900	70	100	1450	8.5	1.3498	0.0125				
	7	1300	0.7	0	0	100	900	70	100	3916	8.1	1.4736	0.0023				
	8	1300	0.7	0	0	100	900	70	100	2008	8.3	1.3587	0.0075				
	9	1300	0.7	0	0	100	900	0	100	3965	22.1	1.5007					
	10	1300	0.7	0	0	100	900	0	100	2097	22.5	1.3749	0.005				
	11	1300	0.7	0	0	200	900	5	100	1392	13.5	1.4871	0.005				
Pot Refilled 24/05/99	12	800	0.5	0	0	100	900	70	100	716	13.9	1.374	0.005				
	13	800	0.4	0	0	500	900	70	100	1176	27.3	1.4831	0.0106				
	14	800	0.4	0	0	250	900	70	100	738	25.6	1.4064	0.025				
	15	800	0	0	0	500	900	70	100	2000				0.0343	0	0.1062	
	16	800	0	0	0	250	900	70	100	-10000	-30			0.0191	0	0.0069	
	17	800	0	0	0	250	900	70	100	100	1.45						
	18	800	0	0	0	250	900	70	100	5200							
	19	800	0	0	0	250	900	70	100	7200							
	20	800	0	0	0	250	900	40	100	5338	23.4	1.4938					
	21	800	0	0	0	250	900	40	100	4200							
	22	800	0	0	0	250	900	20	100	3641	14.4	1.4913	0.015				
	23	800	0	0	0	250	900	20	100	6500							

Fig. 6

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Process Parameter										Bulk Film Properties				Comment			
Run Number	CHMMS (g/min)	O ₂ Flow (Sccm)	N ₂ Flow (Sccm)	Pressure (mT)	Power (W)	Showerhead (°C)	Platen (°C)	Dep rate (Å/min)	Uniformity (%)	Refractive Index	Dielectric Constant	SiC/SiO	SiH/SiO	CH/SiO	FTIR P.A.R		
1	0.65	0	0	900	250	100	50	7224	10.6	1.4619	0.03577	0.01111	0.1347	ACT 1000mL, slight stn			
2	0.65	0	0	900	250	100	50	-	-	-	0.03453	0.0296	0.03672	Pealed off in FTS			
3	0.65	0	100(1+8)	900	250	100	50	8190	6.5	1.4875	0.039	0.015	0.1545	Plasma dark red			
4	0.65	0	50(1+8)	900	250	100	50	5810	22.8	1.4652	0.0354	0.0269	0.3499	Purple Plasma			
5	0.65	0	50(1+8)	900	250	100	50	8289	13.1	1.51	0.0384	0.0107	0.131				
6	0.65	0	50(1+8)	900	250	100	50	8906	4.7	1.5089	0.0379	0.0139	0.1238				
7	0.65	0	100(1+8)	900	250	100	50	8717	2.37	1.4475	0.0364	0.0172	0.1886				
8	0.65	0	100(1+8)	900	100	100	50	2789	9.2	1.4775	0.0349	0.0367	0.3518	RI wafer			
9	0.65	0	100(1+8)	900	300	100	50	12748	3.4	1.489							
10	0.85	0	100(1+8)	900	500	100	50	14222	1.77	1.538							
11	0.85	0	200(1)	900	500	100	50	14192	1.5	1.5228							
12	0.85	0	200(8)	900	500	100	50	14282	1	1.5444							
13	0.85	0	100(1+8)	500	500	100	50	9790	3.7	1.4895							
14	0.85	0	100(1+8)	500	500	100	50	11382	6.2	1.4468							
15	0.85	0	200(8)	900	500	100	50	19116	5.6	1.4634							
16	0.65	0	100(1+8)	900	250	100	50	10242	6.6	1.4558							
17	0.65	0	100(1+8)	900	250	100	50		3°								
18	0.85	0	200(8)	800	500	100	50		2.78°								
19	0.85	0	100(1+8)	500	500	100	50		2.82°								
20	0.65	0	100(1+8)	900	500	100	50		3.01°								
21	0.85	0	100(1+8)	900	500	100	50	7869	7.8	1.5144							
22	0.85	0	100(1+8)	900	500	100	50	15697	5.7	1.5387							
23	0.85	0	100(1+8)	800	500	100	50	14731	3.5	1.4737							
24	0.85	0	100(1+8)	900	500	100	50	14345	0.9	1.4737							
25	0.85	0	100(1+8)	900	500	100	50	14079	1.6	1.4582							
26	0.85	0	200(8)	900	500	100	50	18864	4.5	1.4332							
27	0.85	0	200(8)	800	750	100	50	17841	7.2	1.4327							
28	0.85	0	200(8)	900	250	100	50	11511	6.3	1.4263							
29	0.85	0	200(8)	800	500	100	50	15365	3.5	1.4856							
30	0.85	0	200(8)	900	500	100	50	14807	3.1	1.4575							
31	0.85	0	200(8)	900	750	100	50	16898	3.8	1.503							
32	0.85	0	200(8)	900	250	100	50	11658	11.5	1.499							
33	0.85	0	200(8)	900	500	100	50		2.56								
34	0.85	0	200(8)	900	300	100	50		2.66								
35	0.85	0	200(8)	900	300	100	50	17106	3.7	1.4552							
36	0.85	0	200(8)	900	500	100	50	17194	3.7	1.458							
37	0.85	0	200(8)	1200	500	100	50	24708	2.2	1.5316							
38	0.85	0	200(8)	600	500	100	50	9953	1	1.5109							
39	0.85	0	200(8)	600	250	100	50	7128	0.87	1.5298							
40	0.85	50	150(8)	900	250	100	50	9652	3.8	1.4575							
41	0.85	50	150(8)	900	300	100	50	18448	3.8	1.4209							

Fig. 7 (Part 1 of 3)

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Run Number	CHMMS (g/min)	O ₂ Flow (Sccm)	N ₂ Flow (Sccm)	Pressure (mT)	Power (W)	Showerhead (°C)	Platen (°C)	Dop rate (Admin)	Uniformity (%)	Refractive Index	Dielectric Constant	SICASIO	SIHSIO	CHSIO	Comment
42	0.85	50	250[8]	900	500	100	50	-1.8μm	-	0.0209	0.0058	0.0572	Entire film cloudy		
43	0.85	200	0	900	300	100	50	17888	5.2	1.3978	0.0161	0.003	0.0356	Powder stripes	
44	0.85	50	150[8]	900	1000	100	50	17896	6.4	1.3031	0.0145	0.0068	0.0588	Hazy powder	
45	0.85	0	200[8]	600	250	100	50	8213	3.4	1.4659	0.0378	0.0164	0.2189	RI Wafer	
46	0.85	0	200[8]	600	250	100	50	9912	8.2	1.4649				RI Wafer	
47	0.85	0	200[8]	1200	100	100	50	1792	29.2	1.4635				RI Wafer	
48	0.85	0	200[8]	600	250	100	50	10233	3.3	fix	0.0187	0.0516	0.3823	No FTS	
49	0.85	0	200[8]	600	250	100	50			2.56				5min FTS, no cap	
50	0.85	0	200[8]	800	250	100	50			2.72				Wafer thin, 1st of day, 5min FTS, Cap	
51	0.85	0	200[8]	900	250	100	50			3.16				No FTS	
52	0.85	0	200[8]	900	250	100	50			2.33				30min FTS, Cap	
53	0.85	0	200[8]	900	250	100	50	13034	5.7	fix	0.0371	0.0532	0.3933	No FTS	
54	0.85	0	200[8]	900	250	100	50	13829	5.7	fix	0.0367	0.0599	0.3885	No FTS	
55	0.85	0	200[8]	800	250	100	50	11131	7.7	fix	0.0368	0.0135	0.151	5min FTS	
56	0.85	0	200[8]	900	250	100	50	9808	4.9	fix	0.0376	0.0101	0.0785	30min FTS	
57	0.85	0	200[8]	900	250	100	50	9853	3.4	fix	0.0363	0.0082	0.0383	60min FTS	
58	0.85	0	200[8]	900	250	100	50			2.62				5min FTS, no cap	
59	0.85	0	200[8]	900	250	100	50			2.55				30min FTS, no cap	
60	0.85	0	200[8]	900	250	100	50			2.52				60min FTS, no cap	
61	0.85	0	200[8]	900	250	100	50	13020	8.1	1.5351	0.0374	0.0551	0.3939	No FTS	
62	0.85	0	200[8]	900	250	100	50	12801	7.2	1.3638	0.0367	0.0573	0.3911	No FTS	
63	0.85	0	200[8]	900	250	100	50	12430	6.5	1.4763	0.0322	0.02	0.2575	5min FTS @ 500°C	
64	0.85	0	200[8]	900	250	100	50	11885	4.2	1.4466	0.0345	0.0126	0.1847	30min FTS @ 500°C	
65	0.85	0	200[8]	900	250	100	50	10679	137	1.3553	0.0373	0.0102	0.109	60min FTS @ 500°C	
66	0.85	0	200[8]	900	250	100	50			2.93				5min FTS @ 500°C no cap	
67	0.85	0	200[8]	900	250	100	50			2.97				5min FTS, cap @ 500°C	
68	0.85	0	200[8]	900	250	100	50			2.61				60min FTS, cap @ 500°C	
69	0.85	0	200[8]	900	500	100	50	17388	4.2	1.4207	0.0333	0.0111	0.094	30min FTS	
70	0.85	0	200[8]	900	500	100	50	17484	3.8	1.4148	0.0323	0.0103	0.0825	60min FTS	
71	0.85	0	200[8]	900	500	100	50			2.55				30min FTS, cap	
72	0.85	0	200[8]	900	500	100	50			2.53				60min FTS, cap	
73	0.85	50	200[8]	900	250	100	50	9869	4.3	1.4218	0.0306	0.0073	0.0635	5min FTS (centre cracks)	
74	0.85	50	150[8]	900	250	100	50	9564	4.2	1.3767	0.0298	0.0064	0.0403	30min FTS, no cracks	
75	0.85	50	150[8]	900	250	100	50			2.26				30min FTS, cap	
76	0.85	0	200[8]	900	250	100	50	13971	6	1.4022				RI Wafer	
77	0.85	0	200[8]	900	250	100	50	12355	8.3	1.4308				RI Wafer	
78	0.85	50	150[8]	900	250	100	50	11928	6.1	1.4115				RI Wafer	
79	0.85	50	150[8]	900	250	100	50	11070	6.9	1.3942				RI Wafer	
80	0.85	0	200[8]	900	500	100	50	23340	7.4	1.4493				RI Wafer	
81	0.85	0	200[8]	900	500	100	50	22157	6.5	1.4307				RI Wafer	
82	0.85	0	200[8]	900	500	100	50	17612	3.4	1.4354				5min FTS	
83	0.85	0	200[8]	900	500	100	50	17736	2.7	1.3128				No FTS	
84	0.85	0	200[8]	900	500	100	50	14838	2.4	1.4463				30min FTS	
85	0.85	0	200[8]	900	500	100	20	21774	6.8	1.5383				No FTS	
86	0.85	0	200[8]	900	500	100	20			0.036				30min FTS (peeled off)	
87	0.85	0	200[8]	900	500	100	20			0.0349				60min FTS (peeled off)	
88	0.85	0	200[8]	900	500	100	20			2.43					

Fig. 7 (Part 2 of 3)

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Run Number	CHMMs (g/min)	O ₂ Flow (Sccm)	N ₂ Flow (Sccm)	Pressure (mT)	Power (W)	Showhead (°C)	Platen (°C)	Dop rate (Å/min)	Uniformity (%)	Refractive Index	Dielectric Constant	SiC/SiO	FTIR P.A.R.	Comment
89	0.85	0	200(8)	900	500	100	50	17.144	2.4	1.4129	0.0341	0.0103	0.1051	
90	0.85	2.5	175(8)	900	500	100	50	17.840	1.9	1.4398	0.027	0.0073	0.0776	Feint powder si/h
91	0.85	2.5	175(8)	900	250	100	50	9279	2.4	1.3875	0.0327	0.0079	0.0725	
92	0.85	50	150(8)	900	250	100	50	3663	5.9	1.3646	0.0308	0.0065	0.0456	Small amount of centre cracking
93	0.85	50	0	900	500	100	50	-100000			0.0344	0.0079	0.0532	Massive centre cracking
94	0.85	50	0	900	500	100	50	21408	4.6	1.4199	0.0273	0.0076	0.0725	
95	0.85	50	150(8)	900	250	100	50			2.49			30min FTS, cap	
96	0.85	50	150(8)	900	250	100	50			2.48			30min FTS, cap	
97	0.85	2.5	175(8)	900	250	100	50	9917	8.8	1.4521	0.0342	0.0093	0.1091	5min FTS
98	0.85	2.5	175(8)	900	250	100	50	9848	11.7	1.4592	0.0334	0.0117	0.1441	5min FTS
99	0.85	2.5	175(8)	900	250	100	50			2.437			5min FTS, cap	
100	0.85	2.5	175(8)	900	250	100	50			2.286			60min FTS, cap	
101	0.85	2.5	175(8)	900	250	100	50			2.426			30min FTS, cap	
102	0.43	0	100(8)	900	500	100	50	12080	7.6	1.5107	0.0239	0.0093	0.096	5min FTS Showerhead dots
103	0.43	0	100(8)	900	500	100	50	12502	5.1	1.5081	0.025	0.0118	0.0116	5min FTS Showerhead dots
104	0.64	0	150(8)	900	500	100	50	20470		2.9			30min FTS cap	
105	0.85	0	400(8)	900	750	100	50	14014	3.5	1.4983	0.0282	0.0149	0.0912	5min FTS
106	0.85	0	400(8)	900	750	100	50	13930	2.4	1.496	0.0278	0.0143	0.0771	30min FTS
107	0.85	0	400(8)	900	750	100	50			2.72			30min FTS CAP	
CHAMBER SPACING CHANGED TO 20MM														
108	0.85	0	200(8)	900	500	100	50	17626		1.3437			30min FTS	
109	0.85	0	200(8)	900	500	100	50	21765	8.4	1.3654			30min FTS, RI Wafer L	
110	0.85	2.5	175(8)	900	250	100	50	11436	17.6	1.3713			30min FTS	
111	0.85	2.5	175(8)	900	250	100	50	12828	12.6	1.3898			30min FTS, RI Wafer	
112	0.85	0	200(8)	600	500	100	50	14280	11.1	1.447			30min FTS, RI Wafer	
113	0.85	0	200(8)	600	500	100	50	12185	3.4	1.3756			30min FTS	
114	0.85	0	200(8)	400	500	100	50	9049	2.8	1.4745			30min FTS	
115	0.85	0	200(8)	400	500	100	50	10620	9.6	1.4649			30min FTS, RI Wafer	
116	0.85	0	200(8)	400	500	100	50	9073	3.5	1.4524	0.0255	0.0143	0.0724	30min FTS
117	0.85	0	200(8)	900	500	100	50	14852	2.3	1.4384	0.0343	0.0096	0.0865	30min FTS
118	0.85	0	200(8)	900	500	100	50			2.5556			30min FTS, Cap	
119	0.85	0	200(8)	400	500	100	50			2.76			30min FTS, Cap	
120	0.85	0	200(8)	900	500	100	50	11633	1.4334	0.0363	0.0094	0.0751	30min FTS, Stress=8.78E8T	
121	0.85	0	200(8)	900	250	100	50	8813	1.399	0.0386	0.0081	0.01019	30min FTS, Stress=7.313E8T	
122	0.85	2.5	175(8)	900	250	100	50	9207	1.3954	0.0329	0.0069	0.0493	30min FTS, Stress=9.858E8T	
123	0.85	50	150(8)	800	250	100	50	10515	1.381	0.0313	0.007	0.0502	30min FTS, Stress=9.325E8T	
124	0.85	15	185(8)	900	250	100	50	10640	1.3807	0.034	0.0051	0.0556	30min FTS, Stress=9.041E8T	
125	0.85	75	125(8)	900	250	100	50	11727	1.3597	0.0295	0.0042	0.0344	30min FTS, Stress=8.544E8T	
126	0.85	100	100(8)	900	250	100	50	12598	1.3481	0.0293	0.0056	0.0336	30min FTS, Stress=8.778E8T	
127	0.85	25	175(8)	900	250	100	50	9206	1.3718	0.0331	0.0061	0.0468	30min FTS, Stress=8.025E8T	
128	0.85	15	185(8)	900	250	100	50			2.414			30min FTS	
129	0.85	75	125(8)	900	250	100	50			2.49			30min FTS	
130	0.85	100	100(8)	900	250	100	50			2.41			30min FTS	
131	0.85	25	175(8)	900	250	100	50			2.48			30min FTS	
132	0.85	35	185(8)	900	250	100	50			2.43			30min FTS	
133	0.85	15	185(8)	900	250	100	50			2.43			30min FTS	
134	0.85	30	170(8)	900	250	100	50			2.45			30min FTS	

Fig 7 (Part 3 of 3)

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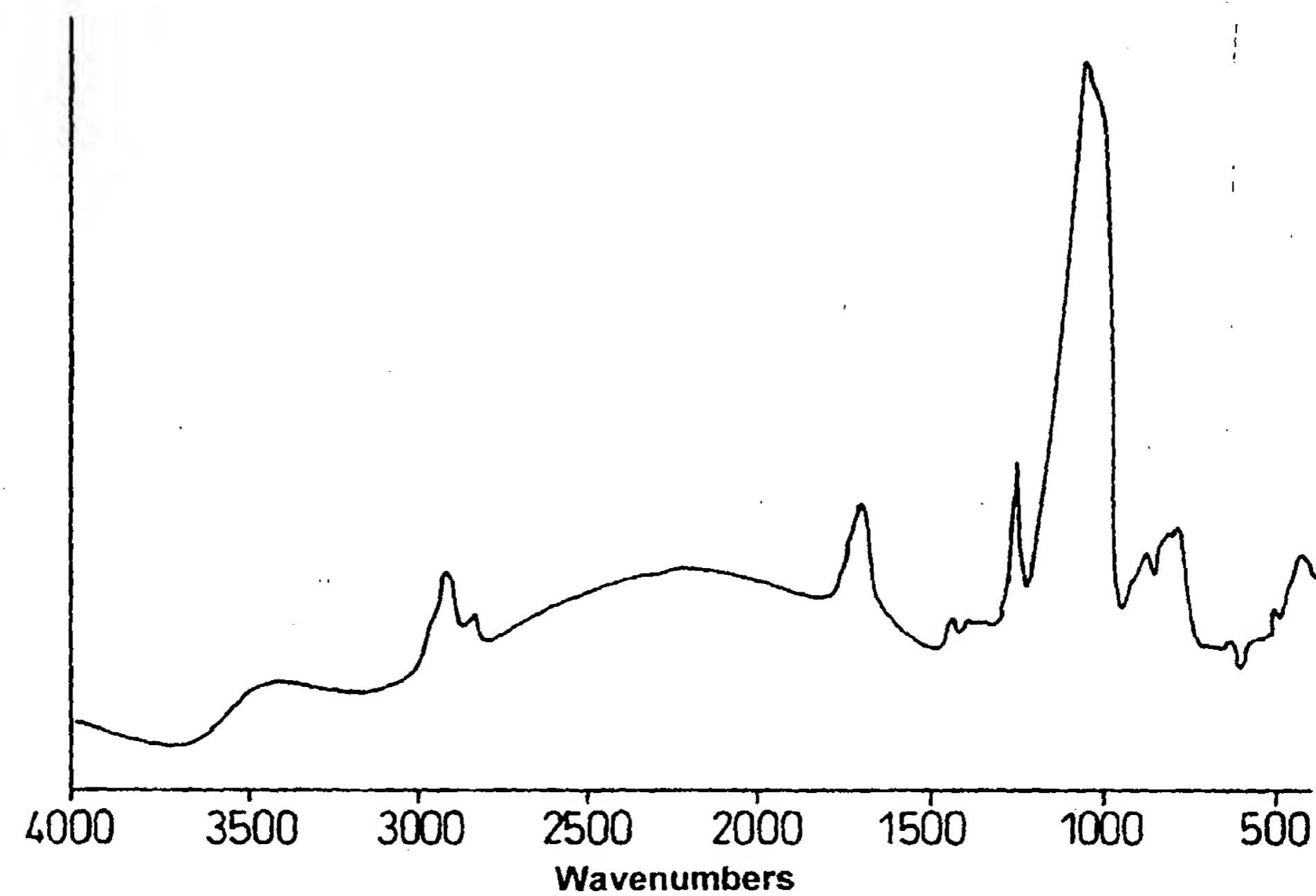
1.) 800CHMMS,0.4g/min H₂O₂, 900mT, 250W as deposited

Fig. 8

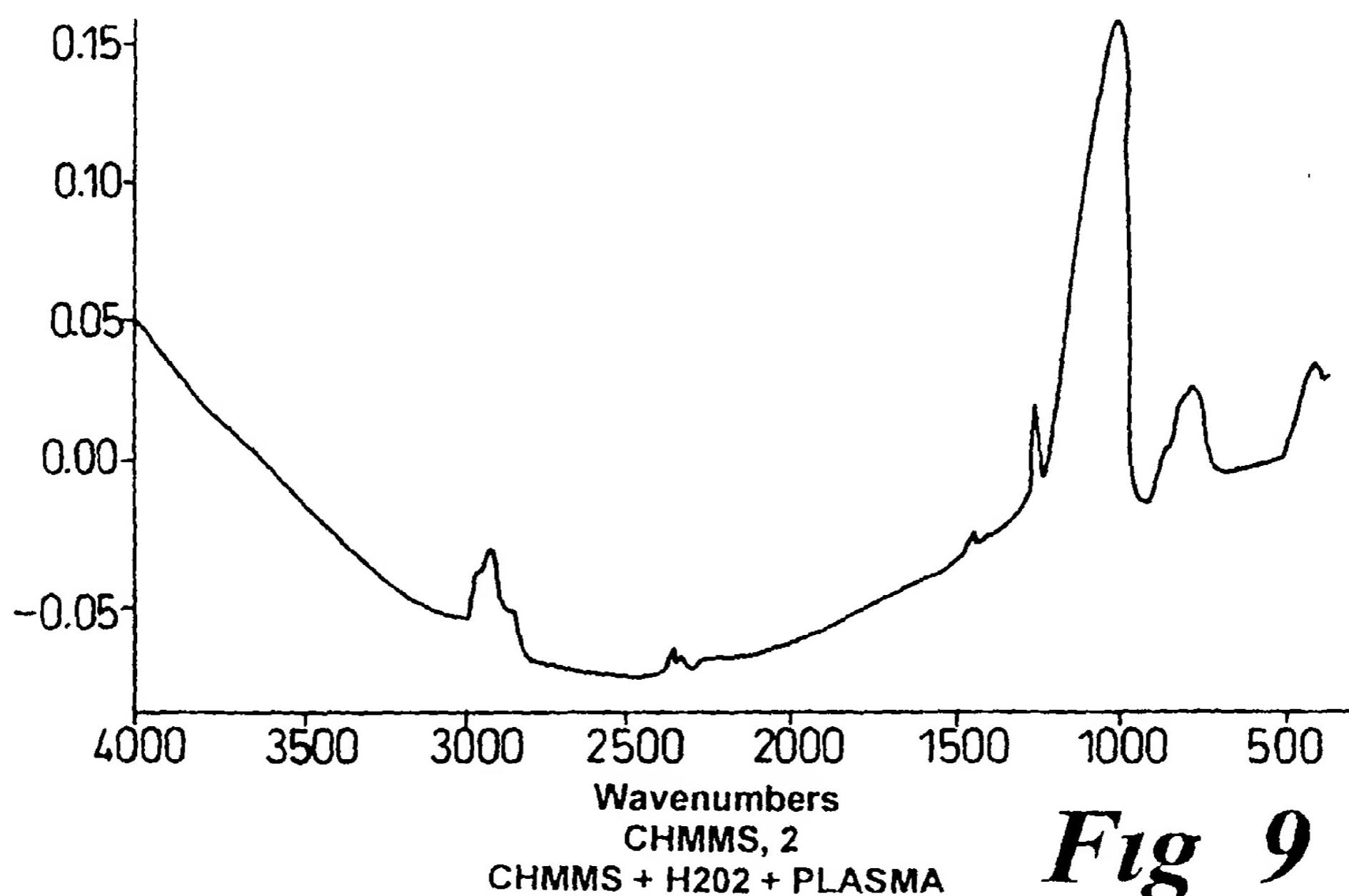
2.) 800Sccm CHMMS, 0.4g/min H₂O₂, 900mT, 500W

Fig 9

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3.) 800Sccm CHMMS, 900mT, 250W

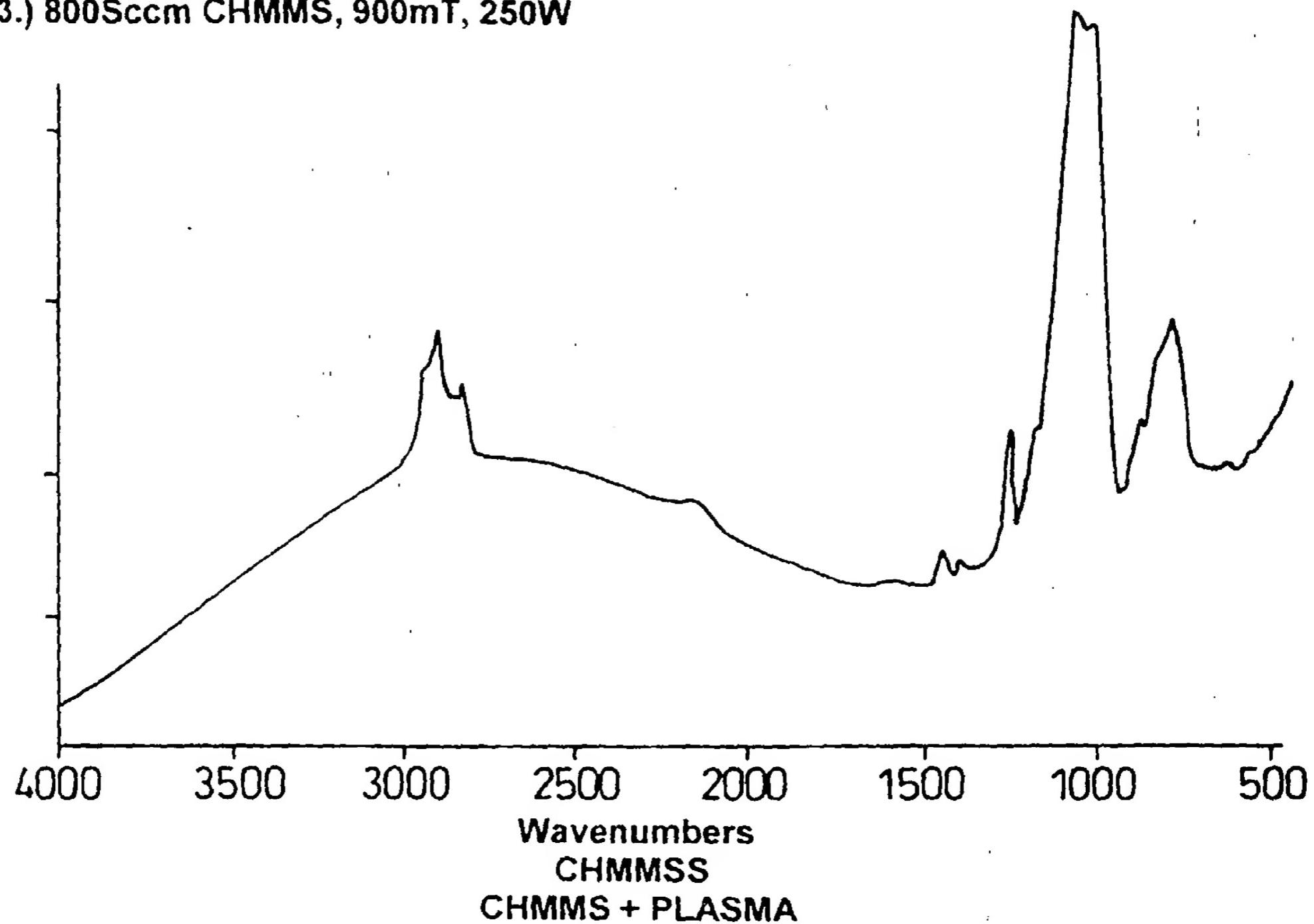
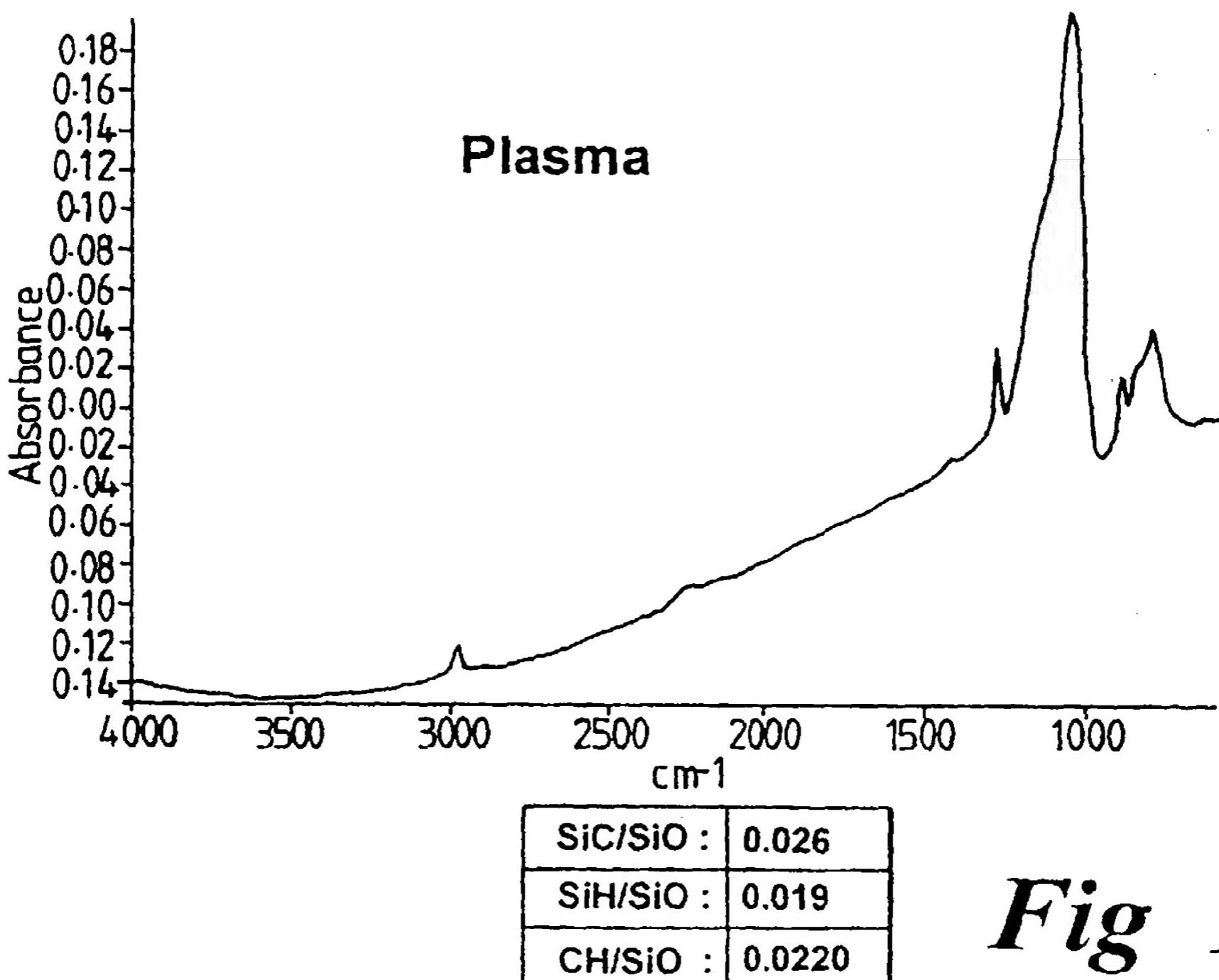
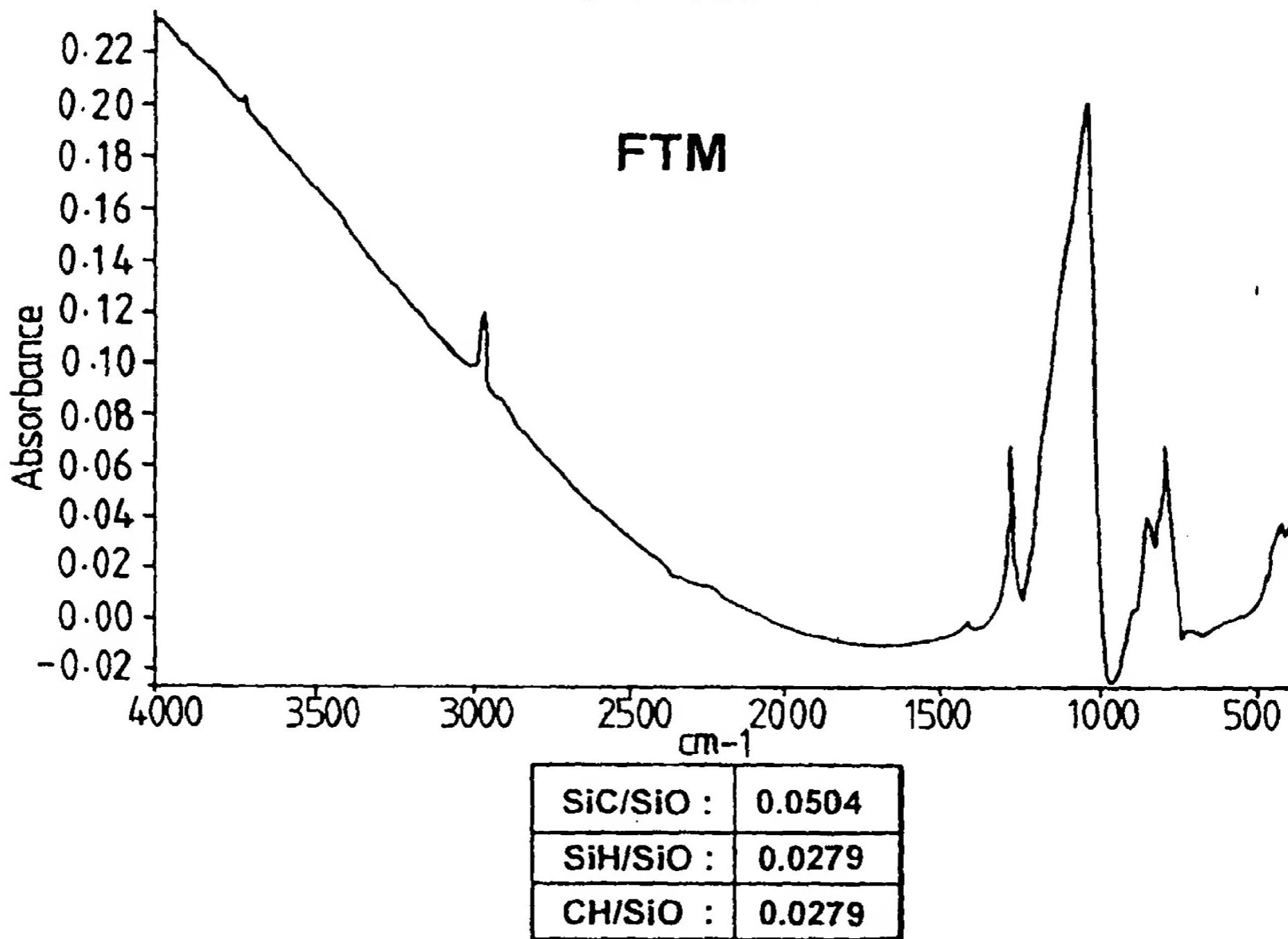
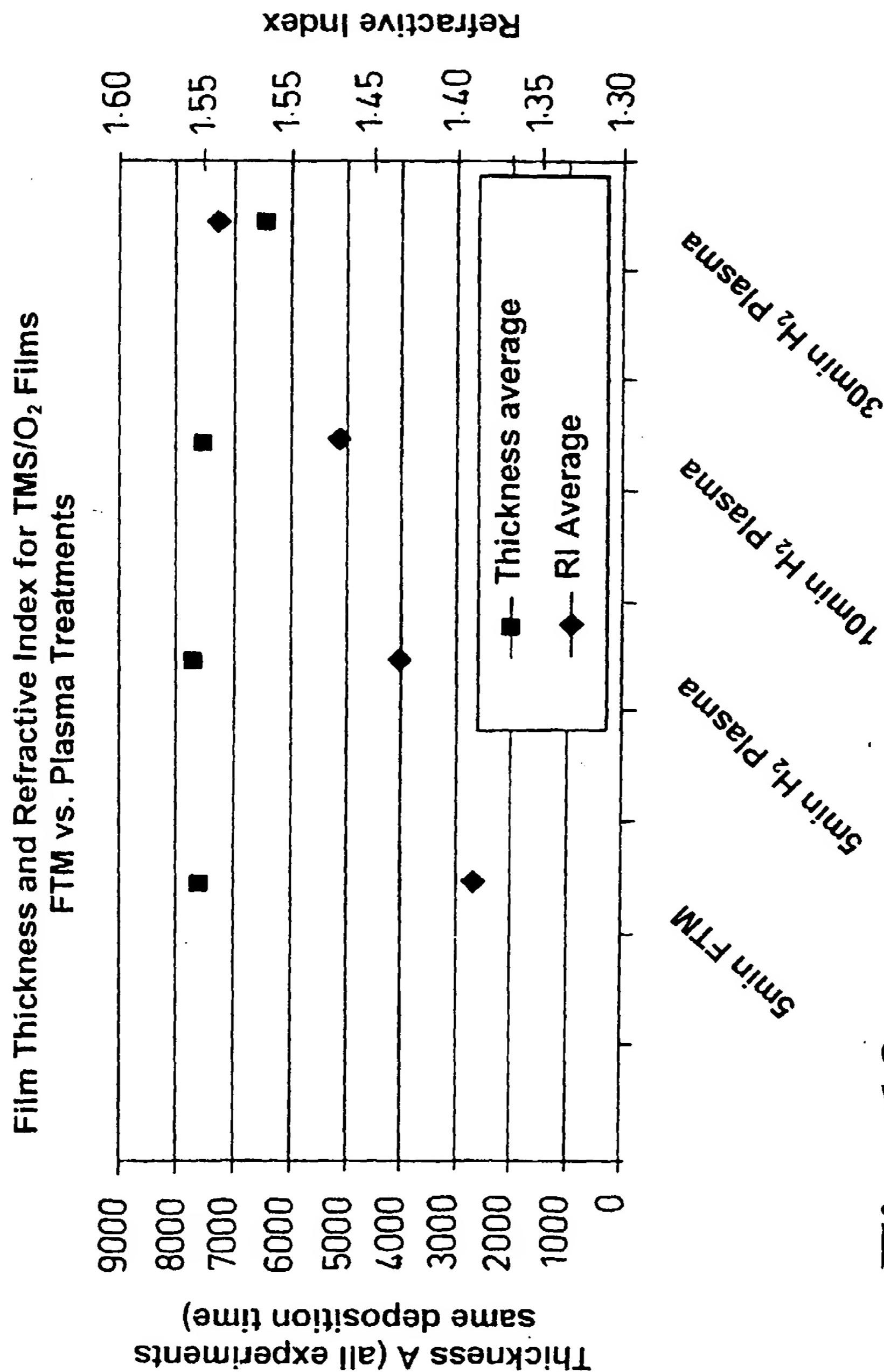


Fig. 10

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**TMS / O₂ Process
FTM v Plasma Treatment – FTIR***Fig 11*

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**Fig. 12**

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TMS / O₂ Process
FTM Treatment – FTIR – oxidising strip resistance

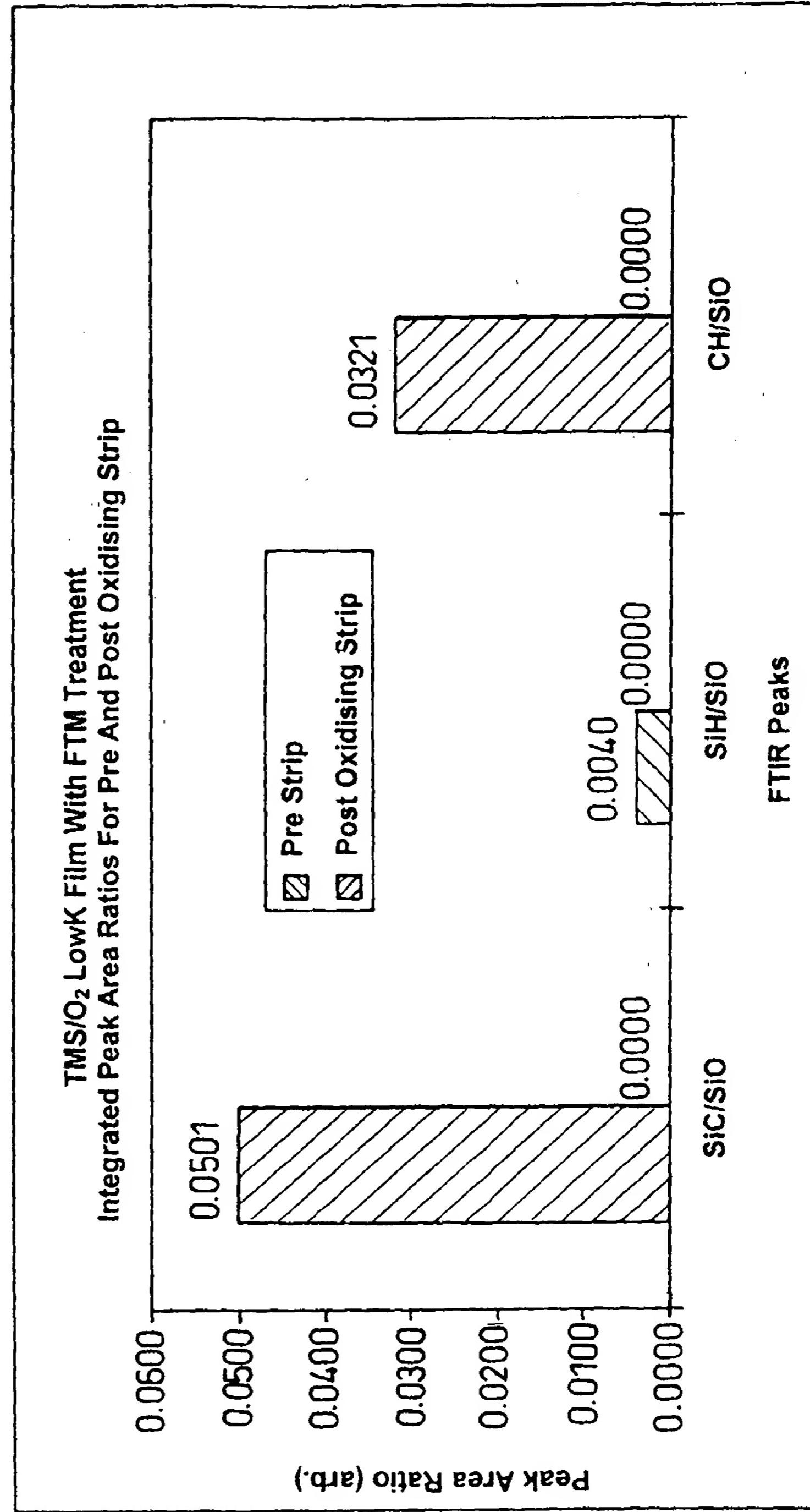


Fig 13

**TMS / O₂ Process
FTM Treatment – FTIR – oxidising strip resistance**

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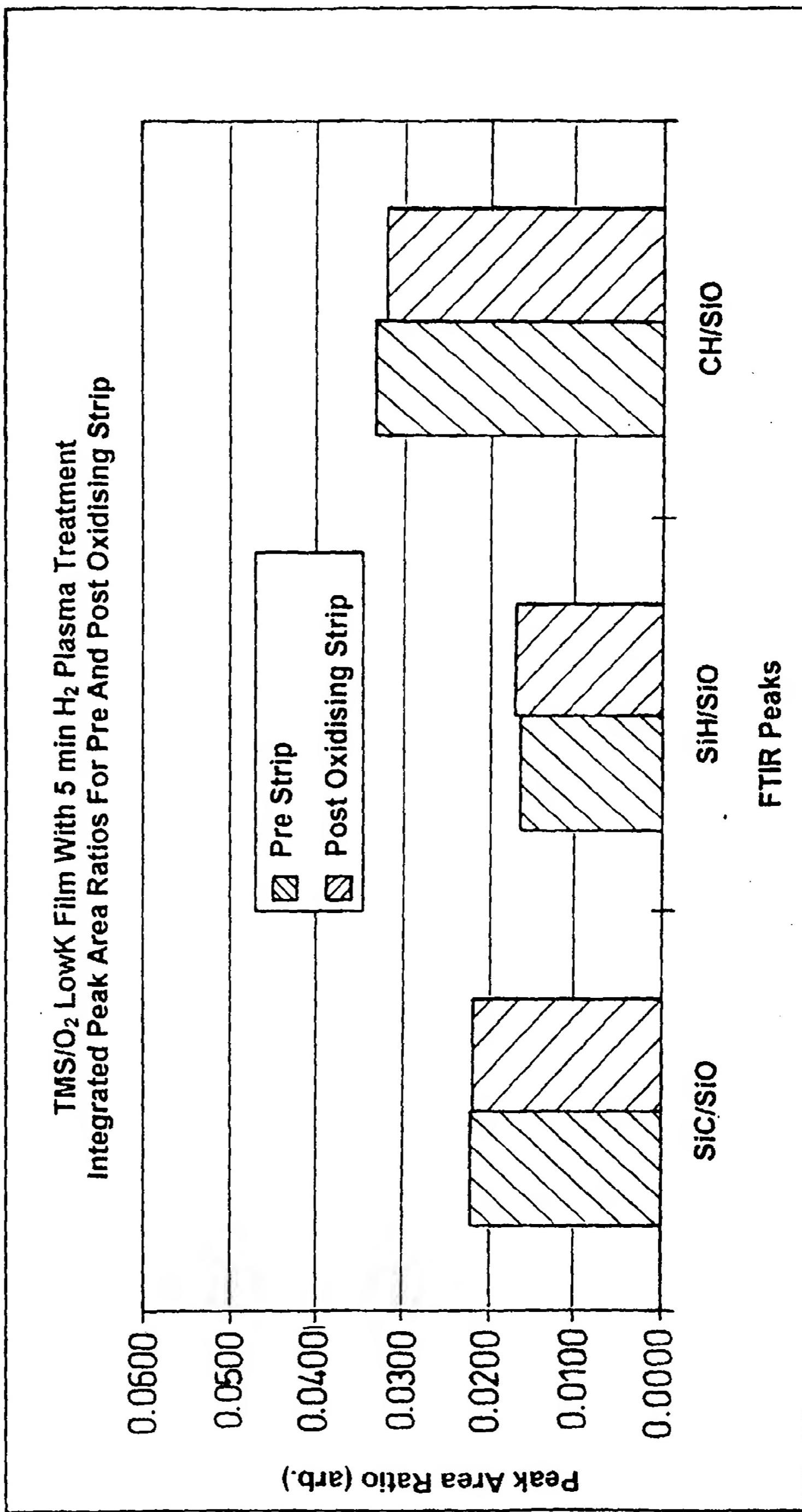


Fig 14

**TMS / O₂ Process
FTM Treatment – FTIR – oxidising strip resistance**

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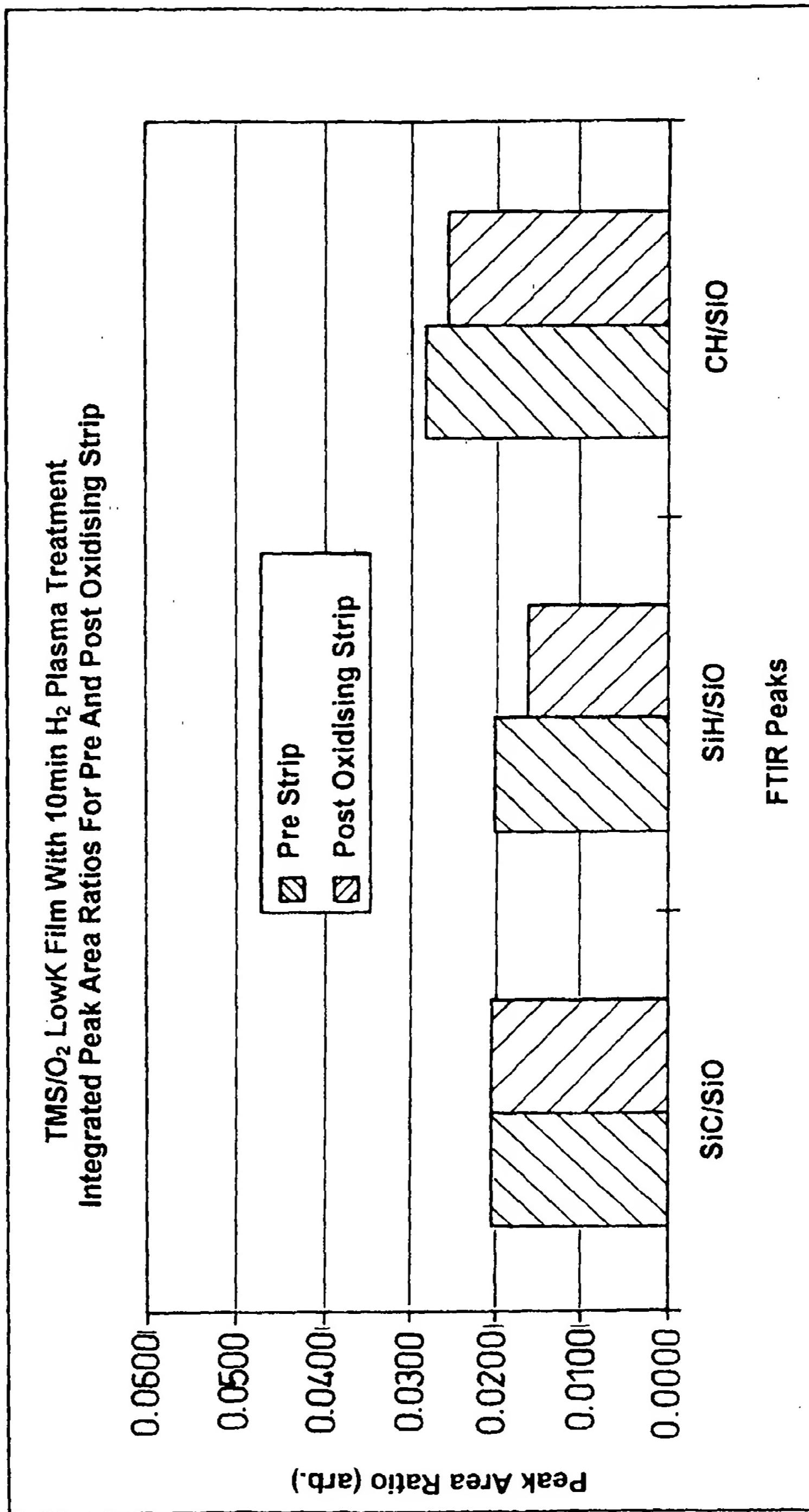


Fig 15

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TMS / O₂ Process
FTM v Treatment stress – oxidising strip resistance

TMS/O₂ LowK Film With FTM and H₂ Plasma Treatment
 Film Stress Values For Pre And Post Oxidising Strip

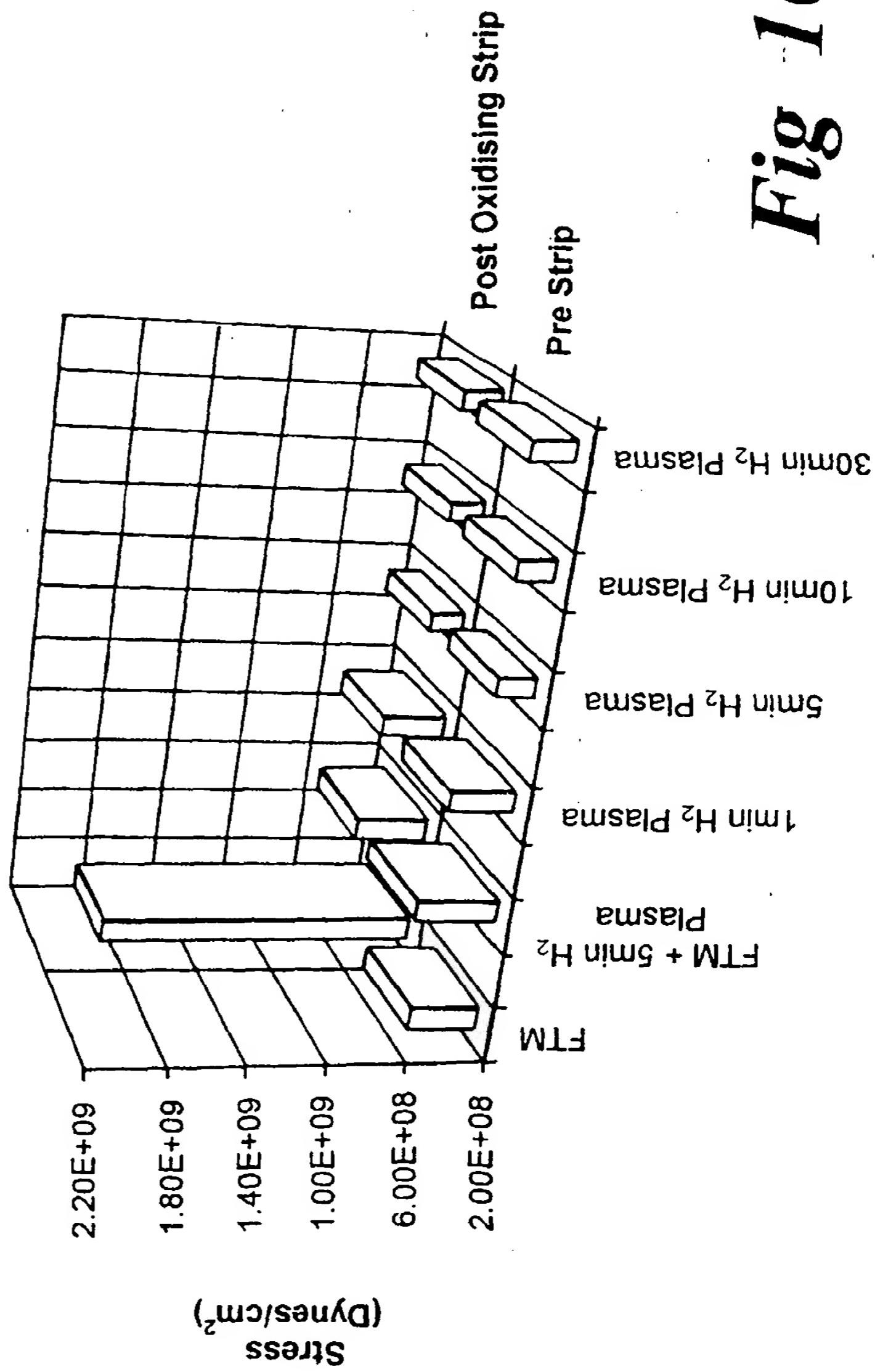


Fig 16

TMS / O₂ Process
Plasma Treatment – Dielectric constant

Dielectric Constant Values For TMS/O₂ Films
FTM and H₂ Plasma Treatments

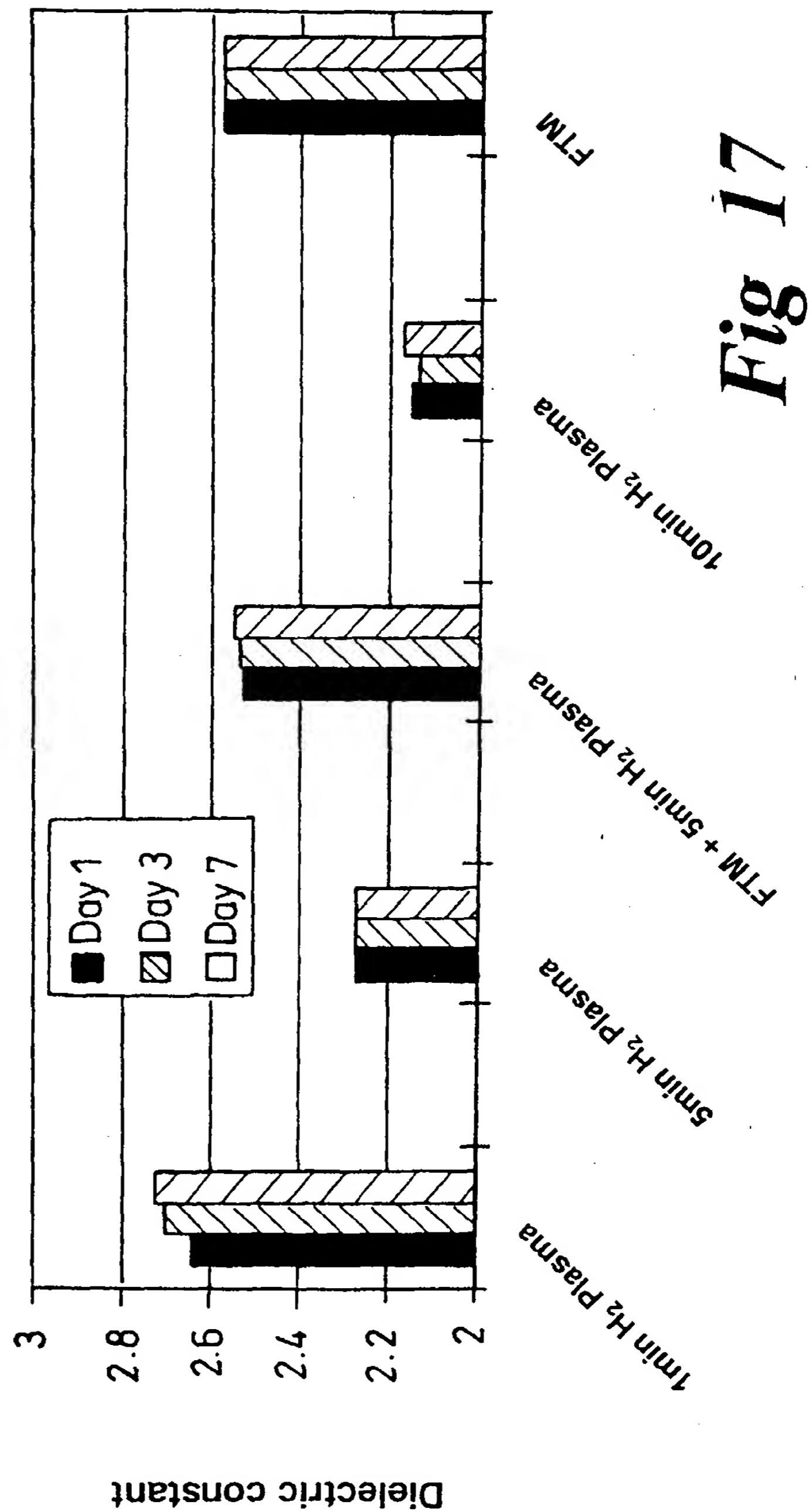


Fig 17

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Dielectric Constant For TMS/O₂ Films
FTM and H₂ Plasma Treatments

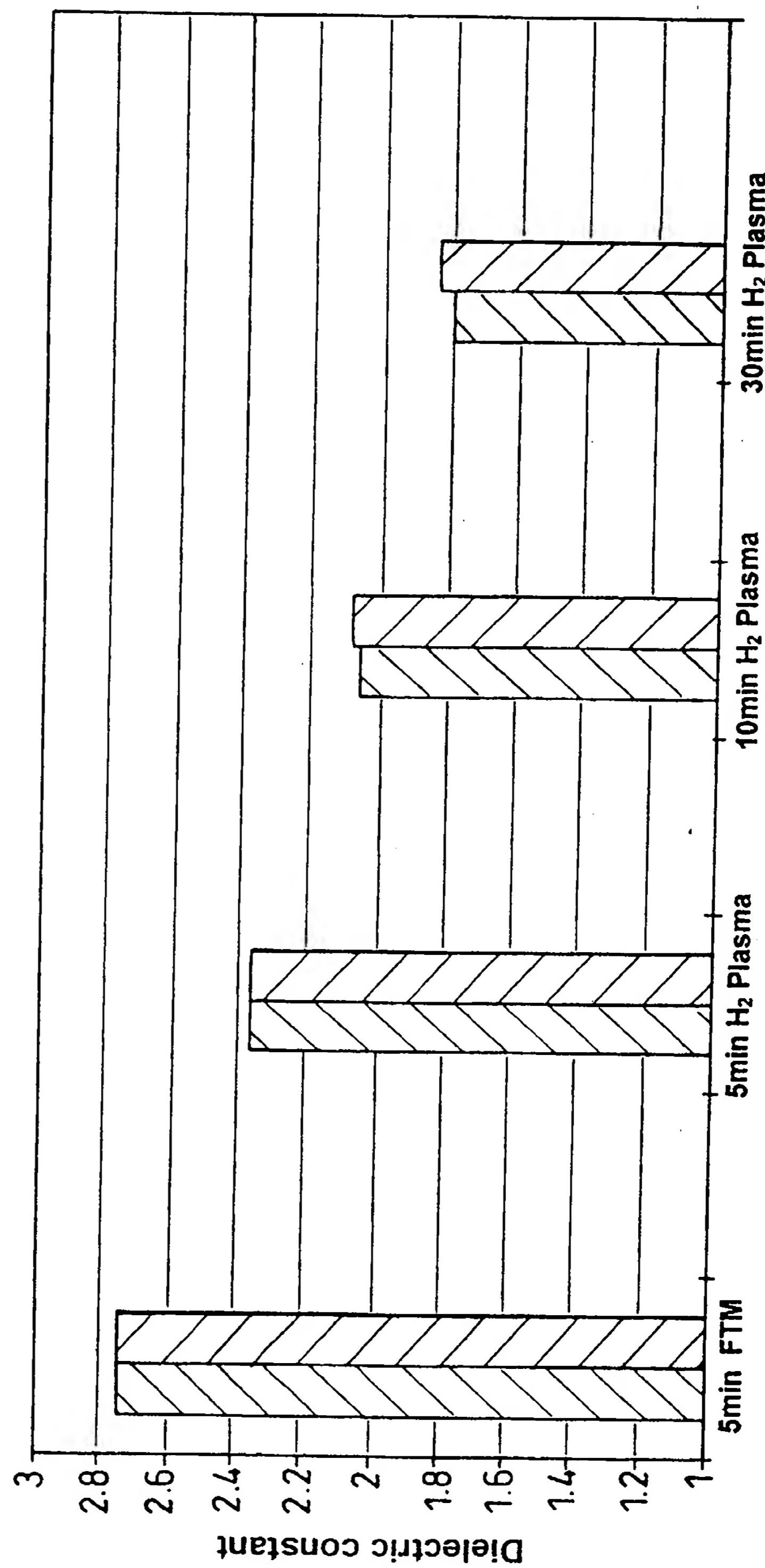


Fig 18

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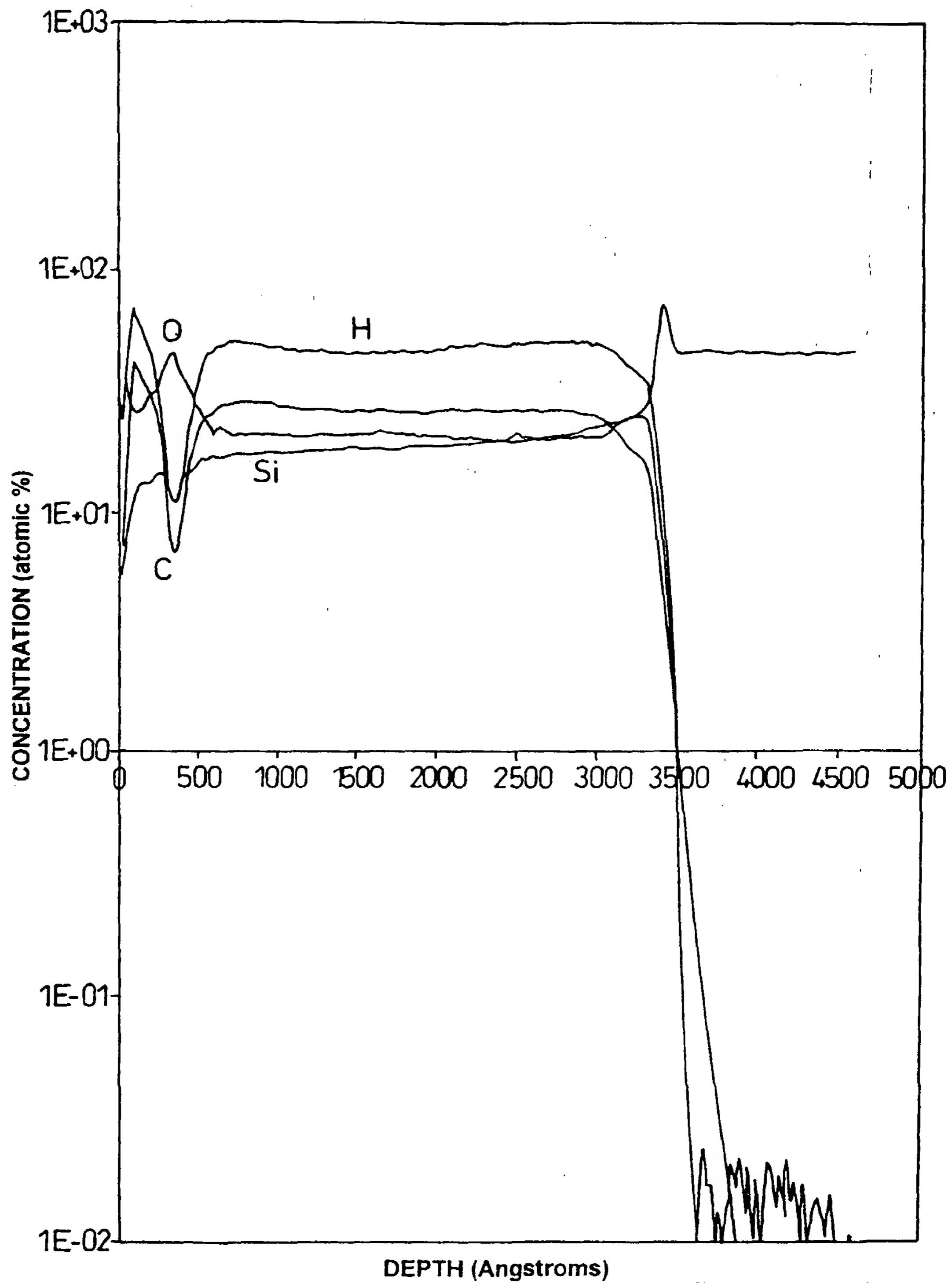


Fig 19

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 00/02301

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01L21/312

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

INSPEC, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GRILL A ET AL: "LOW DIELECTRIC CONSTANT FILMS PREPARED BY PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION FROM TETRAMETHYLSILANE" JOURNAL OF APPLIED PHYSICS, US, AMERICAN INSTITUTE OF PHYSICS, NEW YORK, vol. 85, no. 6, 15 March 1999 (1999-03-15), pages 3314-3318, XP000875752 ISSN: 0021-8979 page 3314 -page 3316 ---	1-5, 8, 9, 11, 13, 24, 25
X	WO 98 08249 A (BEEKMAN KNUT ;KIERMASZ ADRIAN (GB); MCCLATCHIE SIMON (GB); TAYLOR) 26 February 1998 (1998-02-26) same applicant the whole document ---	1, 3, 6, 8, 9, 11, 14, 15, 24-26

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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- "&" document member of the same patent family

Date of the actual completion of the international search

18 September 2000

Date of mailing of the international search report

27/09/2000

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Authorized officer

Szarowski, A

INTERNATIONAL SEARCH REPORT

International Application No
 PCT/GB 00/02301

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 826 791 A (MATSUSHITA ELECTRIC IND CO LTD) 4 March 1998 (1998-03-04)	1,2,11, 14,15, 24,26
A	abstract ---	7
X	EP 0 519 079 A (FUJITSU LTD ;FUJITSU VLSI LTD (JP)) 23 December 1992 (1992-12-23) the whole document ---	1,3-5, 8-11,14, 15,24,26
X	DE 196 54 737 A (TOSHIBA KAWASAKI KK) 3 July 1997 (1997-07-03)	26
A	the whole document ---	1-5, 8-10,12, 13,16, 17,22-25
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 02, 26 February 1999 (1999-02-26) & JP 10 310866 A (SHIN ETSU CHEM CO LTD), 24 November 1998 (1998-11-24) abstract -----	26-29

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int	tional Application No
PCT/GB 00/02301	

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9808249 A	26-02-1998	DE 19781956 T GB 2331626 A		08-07-1999 26-05-1999
EP 0826791 A	04-03-1998	JP 10284486 A US 5989998 A		23-10-1998 23-11-1999
EP 0519079 A	23-12-1992	DE 69130947 D DE 69130947 T WO 9212535 A JP 7093296 B KR 9608508 B US 5314724 A		08-04-1999 08-07-1999 23-07-1992 09-10-1995 26-06-1996 24-05-1994
DE 19654737 A	03-07-1997	JP 9237785 A		09-09-1997
JP 10310866 A	24-11-1998	NONE		